ENHANCED HYDRATE INHIBITORS: POWERFUL SYNERGISM WITH GLYCOL ETHERS

William D. Young, Jeff M. Cohen, and Philip F. Wolf
International Specialty Products
1361 Alps Rd., Wayne, NJ 07470

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INTRODUCTION

Since natural gas hydrates frequently plug oil and gas production lines, various chemical and thermal methods have been developed to prevent hydrate formation. Conventional chemical treatment involves injecting 20-50 weight % methanol in the water phase at the wellhead or downhole to depress the freezing point of hydrates below the minimum fluid temperature in the line. However, high methanol injection rates are expensive and may exacerbate pipeline corrosion. Alternative chemical treatment methods are needed.

Recently Lederhos, et al[1] reported that certain water soluble polymers effectively inhibit hydrates at treatment levels of 0.1 to 1.0 wt% in the water phase, far less than required by methanol. At typical flowline conditions, these polymers slow the rates of hydrate nucleation and growth to such an extent that virtually no hydrates form in the wellstream during transport to processing facilities. Since the polymers slow hydrate formation rather than depress the freezing point, they are called 'kinetic inhibitors.' Under favorable conditions, kinetic inhibitors have prevented hydrates for more than 5 days. Industry field tests have demonstrated the viability of this technology.[2,3]

The most successful of the kinetic inhibitors are vinylcaprolactam (VCL) and vinylpyrrolidone (VP) based polymers, including Gaffix VC-713, a terpolymer of VCL, VP, and dimethylaminoethylmethacrylate (DMAEMA), and PVCL homopolymer. In addition, PVP, although not as effective as VC-713 and PVCL, has been widely used because it costs less and provides adequate protection in less demanding applications.[1,4]

ISP manufactures a full line of hydrate inhibitors including VC-713, PVCL, PVP and VCL/VP copolymers. These inhibitors are tested in the high pressure laboratory at realistic pipeline conditions. We have observed that several glycol ether solvents (for example, 2-butoxyethanol) significantly enhance the performance of the polymeric hydrate inhibitors. Better inhibitors provide lower polymer treatment levels and lower overall cost. This paper presents the results of our experimental study on hydrate inhibitors containing glycol ether solvents.

EXPERIMENTAL

The tests were conducted in a 300 ml stainless steel stirred reactor at high pressure and low temperature. A diagram of the apparatus is shown in Figure 1. Following the procedure of Long, et al,[4] 30 stainless steel balls are placed in the bottom of the reactor to increase nucleation sites. The reactor is immersed in a refrigerated bath, which normally maintains temperature to within 0.5°F. The pressure in the reactor is controlled to within 5 psi by a programmable syringe pump. The pump displaces hydraulic oil into a piston cylinder which contains the hydrate-forming gas on one side and hydraulic oil on the other. The volume of oil displaced by the syringe pump to maintain constant pressure indicates gas consumption in the reactor.

The inhibitors were tested at 0.5 wt% dry polymer and 0.75 wt% glycol ether in the salt solution. In a typical experiment, 0.6 g dry polymer and 0.9 g glycol ether liquid were added to 120 g of a 3.5 wt%, filtered, synthetic sea salt solution and mixed for at least one hour. The resulting solution was transferred to the 300 ml reactor, sealed, and immersed in the temperature bath at 39.2°F (4°C). The pressure was then increased to 1000 psig with green canyon gas and held constant to within about 5 psi with the syringe pump. After the pressure reached 1000 psig, the reactor stirrer was turned on to 1000 rpm. The gas volume, as measured by the syringe pump, and the reactor pressure and temperature were recorded electronically at 1 minute intervals throughout the experiment.

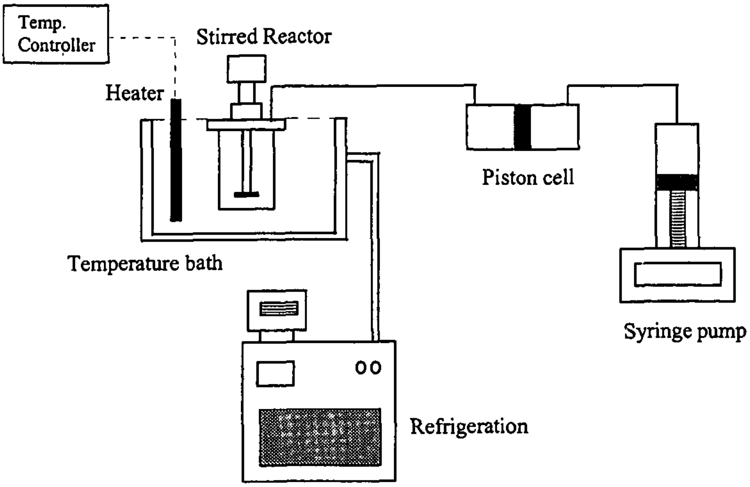

Figure 1: Gas hydrate test apparatus. The 300 ml reactor was charged with 120 g of sea salt solution containing 0.5% dissolved inhibitor. Tests were conducted at constant 39.2°F and 1000 psig for 20 hours. See text for more detail.

MATERIALS

Gaffix VC-713 is a terpolymer of VCL, VP, and DMAEMA. For consistency, all experiments reported here were conducted with the same manufacturing lot of VC-713.

Butyl Cellosolve, or 2-butoxyethanol, has the formula n-$C_4H_9OC_2H_4OH$. It is an industrial solvent with a boiling point of 171°C manufactured by Union Carbide. This material and the other glycol ethers listed in Table 2 were obtained from Aldrich and have a purity of about 99%.

The synthetic sea salt corresponds to ASTM 'Standard Specification for Substitute Ocean Water' and was purchased from Marine Enterprises of Baltimore, Maryland.

Green canyon gas is a typical natural gas mixture. It has the composition listed in Table 1.

Component	Mole %
nitrogen	0.4
methane	87.2
ethane	7.6
propane	3.1
isobutane	0.5
n-butane	0.8
i-pentane	0.2
n-pentane	0.2
total	100

Table 1: Green canyon gas composition

RESULTS AND DISCUSSION

Figure 2 shows the result of adding 0.75 wt% butyl Cellosolve to a mixture of 0.5 wt% VC-713 in sea salt solution. For comparison, the figure also shows the test results for 3.5 wt% sea salt solution with no inhibitor, 0.5 wt% VC-713 in sea salt solution, and butyl Cellosolve in sea salt solution. Each test was conducted at 39.2°F and 1000 psig. At these conditions green canyon gas has an equilibrium dissociation temperature of 64.7°F in deionized water, giving a total subcooling of 25.5°F. The gas consumption was calculated from measured volume change with the real gas law (compressibility factor = 0.83).

As the figure shows, this particular lot of VC-713 inhibits hydrates for only about 40 minutes at the test conditions. Adding 0.75 wt% butyl Cellosolve dramatically increases the performance of the inhibitor, to the extent that no detectable hydrates form for the duration of the 20 hour test. The figure also shows that butyl Cellosolve does not inhibit hydrates without polymer present.

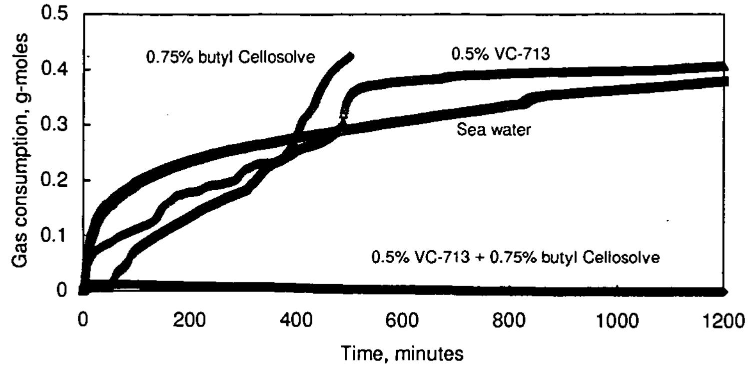

Figure 2: Hydrate inhibition test results at 39.2°F and 1000 psig (subcooling = 25.5°F). The aqueous phase is 3.5 wt% sea salt in all four tests. Concentrations are expressed as weight % in the aqueous phase.

Following up on the result with butyl Cellosolve, other glycol ethers with similar structures were tested at the same concentrations and conditions. Table 2 lists the observed induction times for each material, where induction time has been defined as the time at which detectable gas consumption begins, even if hydrate growth is slow beyond that point.

The data indicate that glycol ethers with 3 or 4 carbons in their alkoxy group significantly enhanced the performance of VC-713. Lower homologs did not appear to have any effect. Higher homologs were insoluble in the salt solution.

Glycol ether	Formula	Induction time (min)
2-butoxy ethanol	n-$C_4H_9OC_2H_4OH$	>1200
2-isopropoxy ethanol	$CH_3CH(CH_3)OC_2H_4OH$	800
1-propoxy-2-propanol	$C_3H_7OCH_2CH(CH_3)OH$	600
2-(2-butoxyethoxy) ethanol	n-$C_4H_9OC_2H_4OC_2H_4OH$	440
1-butoxy-2-propanol	n-$C_4H_9OCH_2CH(CH_3)OH$	450
2-propoxy ethanol	n-$C_3H_7OC_2H_4OH$	350
2-ethoxy ethanol	$C_2H_4OC_2H_4OH$	10
1-methoxy-2-propanol	$CH_3OCH_2CH(CH_3)OH$	10
none (sea water only)		0
none (VC-713 only)		40

Table 2: Induction times for 0.75 wt% glycol ether plus 0.5 wt% VC-713 in 120 g of sea salt water at 39.2°F and 1000 psig.

Butyl Cellosolve also showed strong synergism with other kinetic inhibitors. Table 3 compares the induction times for polyvinylcaprolactam homopolymer (PVCL) and 50/50 VCL/VP copolymer with and without butyl Cellosolve. Test conditions were identical to those described above.

Table 4 lists the surface tension of aqueous solutions of glycol ethers as reported in the manufacturer's literature.[5] The data indicate that the higher homologs are surface active. If this hydrophobicity of the hydrocarbon chain also causes the chain to associate with the dissolved polymer, then the glycol ether may allow the polymer conformation to expand in solution. This could occur if the surfactant breaks the weak bonds between polymer segments which pull the coils together and tighten the conformation. An extended polymer would presumably have more of its length available for interaction with the crystal surface, which may account for its improved performance as a hydrate inhibitor.

	Induction times (minutes)	
Inhibitor (0.5%)	No additive	0.75% butyl Cellosolve
Gaffix VC-713	40	>1200
PVCL	0	>1200
50/50 VCL/VP	0	350

Table 3: Comparison of induction times for kinetic inhibitors with and without butyl Cellosolve added, at 39.2°F and 1000 psig in sea water solution.

Solvent	Mol. weight	Boiling point, °C	Surface tension at 25°C, for 25% aq. solution, by volume (dynes/cm)
methyl Cellosolve	76.1	124.5	54.3
Cellosolve	90.1	134.9	47.1
propyl Cellosolve	104.2	150.1	32.3
butyl Cellosolve	118.2	171.2	28.9

Table 4: Surface tension and other properties of the 2-alkoxy ethanol homologs. All data was obtained from manufacturer's literature.[5]

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