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NOVEL PREDICTION METHODS FOR DRILLING FLUIDS

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1.0 Executive Summary

We developed a new and novel model to predict the hydrate temperature suppression using the resistivity and density of the drilling fluid filtrate. The new model has the following features: (1) useful tool for rapid, on-site determination of gas hydrate temperature suppression in drilling muds; (2) input parameters can be easily measured on site (filtrate resistivity and density at ambient pressure and temperature); (3) valid for drilling fluids inhibited by salts and/or mixtures of salts and glycols; (4) valid for temperature suppression of up to 40°F; (5) except for the type of glycol, no information is needed about the mud composition; (6) valid for glycols and salts concentrations of (0-30 wt%) and (5-26 wt%), respectively.

Our previous model¹ predicted the hydrate temperature suppression of the drilling fluid directly from the composition of the latter. In developing that model, we modified Hammerschmidt's² equation for inhibitor fraction to take into account the effect of mixed inhibitors such as salts and glycerol. In the new model, we further modified Hammerschmidt's² equation to take into account the effect of mixed inhibitors, and developed a method to calculate the inhibitor(s) concentration from the resistivity and density of the drilling fluid filtrate. In developing the new model, we measured the hydrate temperature suppression, resistivity and density of 32 different aqueous solutions. The accuracy of the model predictions is within the range of experimental error.

Both our previous model and the new one will be included in a computer program that will be developed in Phase II of this project.

2.0 Background

Gas hydrate formation during deep-water offshore drilling and production is a well recognized operational hazard. In water depths greater than 1,000 feet (300 m), the sea bed conditions of pressure and temperature become conducive to gas hydrate formation. The DeepStar consortium of major oil companies addressing deep water development problems listed gas hydrates as one of the major technical challenges for deepwater drilling and production. For the past 10 years, Westport Technology Center has been actively involved in the study and mitigation of gas hydrates and has developed analytical equipment, procedures and the technical expertise to address this problem.

Hydrate formation in drilling fluids represents a relatively new experience resulting from the deep-water offshore drilling. Operators are continuously setting record water depths as more reserves are tapped in deep water prospects. As a result, designing suitable drilling fluids that prevent hydrate formation and meet other drilling requirements became an enormous challenge to mud engineers. Few of the hydrate formation incidents that occurred during deep water drilling have been reported by the operators in the open literature³. The first incident took place while drilling offshore the U.S. west coast at water depth of 1150 ft [350 m] with a sea water temperature of 45°F [7°C] at the mudline. The second case took place while drilling a well offshore in the Gulf of Mexico at water depth of 3100 ft [945 m] with mudline temperature of 40°F [4°C]. In both cases hydrates plugged the choke and kill lines during the containment of a gas kick.

A successful kick containment requires that the Blowout Preventer (BOP) operates properly and the choke and kill lines remain clear for circulation. Consequently, knowing, on real time basis, the hydrate formation tendency of the drilling fluid represents a substantial advantage to the driller for safe and successful kick removal. To achieve this objective we developed a new and novel model that can provide real time prediction of the hydrate temperature suppression. This model, which is intended for rig site usage, requires measuring the mud filtrate resistivity and density at ambient temperature. With this input, the model calculates the mud composition and the hydrate temperature suppression. The solids contents of the drilling mud were found to have negligible effect on the hydrate equilibrium conditions⁴.

3.0 Model Development

To predict the hydrate temperature suppression, ΔT , the model first calculates the inhibitor(s) mole fraction, x_{in} from the measured resistivity, R_{mix} and density, ρ_{mix} of the drilling fluid's filtrate. The calculated inhibitor(s) mole fraction, x_{in} is then used in our previous model¹ that predicts the hydrate temperature suppression, ΔT .

3.1 Hydrate Temperature Suppression

The freezing point depression of water is normally expressed by Gibbs-Duhem equation⁵:

$$\ln a_w = -\frac{\Delta h}{RT} \left(1 - \frac{T}{T_0}\right) + \frac{\Delta C_p}{R} \left(\frac{T_0 - T}{T}\right) - \frac{\Delta C_p}{R} \ln\left(\frac{T_0}{T}\right) \quad (1)$$

Where, a_w is the water activity, R is the universal gas constant, T_0 is the ice quadruple point or the hydrate equilibrium temperature of pure water, and T is the freezing point or the hydrate equilibrium temperature of the inhibited solution. The difference in enthalpy, Δh and heat capacity, ΔC_p are assumed constant within the range of calculation. From Equation 1 and other thermodynamic principles, we were able to express¹ the hydrate temperature suppression ΔT , as a third degree polynomial in terms of the inhibitor(s) mole fraction x_{in} :

$$\Delta T = a_1 x_{in} + a_2 x_{in}^2 + a_3 x_{in}^3 \quad (2)$$

In the current model, the mole fraction of the mixed inhibitors (salts and glycols), x_{in} is determined from the following expression:

$$x_{in} = \frac{(\alpha + 1) \frac{w_s}{M_s} + \frac{w_a}{M_a}}{\frac{w_s}{M_s} + \frac{w_a}{M_a} + \frac{w_w}{M_w} - \epsilon} \quad (3)$$

Where α is the degree of ionization of an equivalent solution of salt in water. The concentration of salt in the equivalent solution is allowed to vary so that the inhibitor fraction matches that of the mixed salts and glycol solution. In Equation 3, we introduced the mixing coefficient, ϵ to account for the interaction between mixed inhibitors.

$$\epsilon = \frac{62.203 M_w}{w_w} \left(\frac{w_s w_a}{M_s M_a} \right) - 10.06 \left(\frac{100 - 3.49 w_s}{w_w} \right) \sqrt{\frac{w_s w_a}{M_s M_a}} \quad (4)$$

For solutions of single inhibitors, ϵ becomes zero and Equation 3 converges to the well-known Hammerschmidt's² equation. Detailed derivation of Equation 3 is given in Appendix A.

3.2 Mixture Resistivity

Since no information is available about the type of salts present in the drilling fluid we substituted the actual salt solution with an equivalent NaCl solution that has the same resistivity. This substitution is justified by the fact that the solution resistivity is mainly dependent on the concentration of the free ions in the solution and almost independent of the type of ions. The weight fraction of NaCl in the equivalent solution, which may differ from that of the actual salt, is calculated from the measured resistivity and density of the drilling fluid. This approximation is valid for solutions of mixed salts and glycols as long as the concentration of salts other than NaCl is within 10-15 wt%.

The effect of glycol on the resistivity of the salt solution can be described with the following equation⁶:

$$R_{mix} = \frac{10}{\lambda_{mix} c} = R_w \left(\frac{\lambda_w}{\lambda_{mix}} \right) \quad (5)$$

Where c is the ionic concentration and R_w is the resistivity of the actual salt or the equivalent NaCl concentration in water. λ_{mix} and λ_w are the specific conductivities of the mixed salt-glycol solution and the salt solution, respectively. The ratio $(\lambda_w/\lambda_{mix})$ is a correction factor that takes into account the effect of the glycol on the resistivity of the salt solution. This factor is expressed in the form shown by Equation 6 and referred to with the symbol B .

$$R_{mix} = R_w \exp(B) \quad (6)$$

$$B = b_1 \beta_1 + \frac{b_2}{(1 + \beta_2)} + \frac{b_3}{(1 + \beta_2)^2}$$

$$\beta_1 = \frac{\rho_{mix} w_a}{(\rho_a - \rho_w)} \quad \text{and} \quad \beta_2 = \frac{w_w M_a}{w_a M_w}$$

$$b_1 = 0.94126 * 10^{-3}$$

$$b_2 = 6.38052$$

$$b_3 = 8.79405$$

The correction factor B is a function of the glycol mole fraction and the difference in density between water and glycol. The constants b_1 , b_2 , and b_3 are parameters obtained from fitting measured resistivity data of NaCl and glycol aqueous solutions in the temperature range of 35°F to 78°F. Detailed description of the hydrate temperature suppression determination from the resistivity of the aqueous solution is given in Appendix B.

3.3 Mixture Density

The density of the aqueous solution of mixed salts and glycols is given by the following relationship:

$$\rho_{mix} = \frac{(w_a + w_w)}{\left(\frac{w_a}{\rho_a} + \frac{w_w}{\rho_w}\right)} + Cw_s \quad (7)$$

Where, ρ_a and ρ_w are the densities of glycol and water, respectively. According to Equation 7, the solution density, ρ_{mix} increases with the increase of the weight fraction of the salt, w_s . C is a parameter (equal for most salts up to saturation) that depends on temperature and the weight fraction of the salt in the solution. Equation 8 is the polynomial fit of parameter C to the tabulated⁶ density data of NaCl solution in the temperature range of 32-122°F.

$$C = C_1 + C_2w_s$$

$$C = (7.80979 * 10^{-3} - 1.566 * 10^{-5}T_m + 5.657 * 10^{-8}T_m^2) + 2.418 * 10^{-5}w_s \quad (8)$$

By rearranging Equation 7 the weight fraction of glycol w_a can be expressed as a function of the weight fraction of salt w_s and measured density:

$$w_a = \left(\frac{100 - w_s}{1 - \rho_w/\rho_a}\right) \left(1 - \frac{\rho_w}{\rho_{mix} - Cw_s}\right) \quad (7m)$$

The weight fractions of the equivalent NaCl and glycol are found by solving Eqs. 6, 7m and 8 simultaneously. The calculated weight fractions are used in Equation 3 to determine the inhibitor(s) mole fraction, x_{in} . Finally, the hydrate temperature suppression, ΔT is calculated using Equation 2. To illustrate the calculation procedure, an example is given in Appendix B.

4.0 Experimental Measurements And Procedures

The densities of the solutions were measured at atmospheric pressure using a temperature controlled DMA 48 density meter accurate to 0.1 mg/cc. The sample size was approximately 0.7 cc.

Sample sizes of approximately 12 cc were used to measure the resistivity with a resistivity meter equipped with platinum coated electrodes. The temperature was measured at the center of the sample using a Fluke 52 thermometer accurate to 0.1°C. The resistivity measurements were conducted at atmospheric pressure and temperatures in the range of 32 - 78°F. The measurements are accurate to within 0.001 ohm-m.

The hydrate equilibrium measurements were performed in the device shown in Figure 1. The main component in the test device is a 300 cc Autoclave reactor equipped with a DC motor-driven magnetic mixer and an RPM controller to maintain constant mixing rate. The apparatus is pressure rated to 6000 psi. The reactor is submerged in a glycol bath, temperature controlled by two 1000 Watt immersion heaters and a Blue M PCC 24A-3 immersion cooler. Two Hart Scientific thermistors model 1506, accurate to 0.01°C measured the temperature of the reactor and the bath. Reactor pressure was measured by a Heise 623 pressure transducer with accuracy of 0.1% of full scale.

4.1 Experimental Results And Discussions

Table 1 shows a summary of the experimental data for 32 aqueous solutions of mixed salts and glycols. The table includes both the data measured as part of this work and those previously obtained¹. The concentration of the tested solutions were in the ranges of 0-20 wt% for salt and 0-30 wt% for glycols. The highest hydrate temperature suppression (35.7°F) listed in Table 1 is that of the solution of 20wt% NaCl-10wt% glycol.

Table 1 also includes the resistivity and density measurement for the same solutions conducted at a temperature range of 35°-78°F. Since the model requires that the solution density and resistivity be measured at the same temperature, the resistivity values were interpolated to the temperature of the density measurements.

Table 2 contains the measured hydrate equilibrium conditions for the solutions tested in this work. The data of Tables 1 and 2 were used to determine the hydrate temperature suppression, ΔT and

the corresponding mole fraction of the inhibitor(s), x_{in} for each solution. We used these data in addition to those from our previous work in determining the polynomial coefficients a_1 , a_2 , and a_3 of Equation 2. The last three columns of Table 1 show a comparison between the calculated and measured hydrate temperature suppression. The absolute average deviation of the model prediction is within 1.4°F of the measured values of the hydrate temperature suppression. This value is within the experimental error of the data used in developing the model. Figure 2 shows a plot of the hydrate temperature suppression as a function of the mole fraction of the inhibitor(s). To further verify the model, a field mud sample of unknown composition was tested (sample 32). Using only measured resistivity and density of this mud's filtrate, the model predicted a hydrate temperature suppression of 26.67°F compared to the measured value of 28.92°F.

Table 1- Summary of experimental data and model prediction.

	SALT WT%			ALCOHOL WT%				Temp.	Resistivity	Density	Xin	ΔT	ΔT	Deviation
	NaCl	KCl	CaCl2	Glycerol	EG	FG	AquaCol	T	R	ρ		Calc.	Meas.	
								[°F]	[ohm-m]	[kg/l]	[°F]	[°F]	[°F]	
0											0.0000	0.00	0.00	0.00
1 *	20							77.0	0.0484	1.1456	0.1029	25.30	27.00	-1.70
2	10							77.0	0.0731	1.0687	0.0553	8.56	8.42	0.14
2	10							59.9	0.0875	1.0720	0.0552	8.54	8.42	0.12
2	10							46.4	0.1032	1.0745	0.0551	8.51	8.42	0.09
3	5							77.0	0.1380	1.0326	0.0266	1.77	3.75	-1.98
4	5			5				77.0	0.1390	1.0428	0.0337	3.06	5.12	-2.06
4	5			5				59.9	0.1684	1.0493	0.0359	3.52	5.12	-1.60
4	5			5				46.4	0.1942	1.0512	0.0358	3.50	5.12	-1.62
5 *	20			10				77.0	0.0611	1.1731	0.1273	33.80	35.70	-1.90
6 *			10	10				77.0	0.1039	1.1021	0.0739	14.68	10.10	4.58
7 *			5	5				77.0	0.1549	1.0491	0.0385	4.09	4.00	0.09
8	5			10				77.0	0.1515	1.0572	0.0443	5.48		
9	10			27				77.0	0.1362	1.1399	0.1014	24.76		
10	10			20				77.0	0.1120	1.1210	0.0874	19.58	19.50	0.08
10	10			20				59.9	0.1412	1.1204	0.0823	17.71	19.50	-1.79
10	10			20				46.4	0.1740	1.1279	0.0840	18.30	19.50	-1.20
11			5					77.0	0.1449	1.0401	0.0319	2.69	2.34	0.35
12	5			20				77.0	0.1863	1.0827	0.0630	10.99		
13			5	20				77.0	0.2151	1.0827	0.0637	11.23	8.23	3.00
13			5	20				46.4	0.3048	1.0930	0.0634	11.12	8.23	2.89
14	5			10				77.0	0.1449	1.0573	0.0442	5.46		
15	5			15				77.0	0.1630	1.0706	0.0542	8.24		
16	10			10				77.0	0.0980	1.0989	0.0714	13.83	12.68	1.15
17	5			5				77.0	0.1481	1.0431	0.0341	3.14	5.12	-1.98
18 *		10		10				77.0	0.0817	1.0875	0.0631	11.03	9.10	1.93
19		10						77.0	0.0672	1.0619	0.0507	7.22	6.92	0.30
20		5		10				77.0	0.1505	1.0539	0.0419	4.90	5.66	-0.76
21 *	3	5		5				77.0	0.1034	1.0635	0.0475	6.34	7.60	-1.26
22 *	10				10			77.0	0.1101	1.0825	0.0767	15.69	16.80	-1.11
22 *	10				10			64.4	0.1270	1.0905	0.0804	17.00	16.80	0.20
23 *	5				5			77.0	0.1525	1.0394	0.0392	4.25	6.60	-2.35
25	10			10				77.0	0.0923	1.0950	0.0673	12.42	12.68	-0.26
26 *	20							77.0	0.0489	1.1456	0.1023	25.06	27.00	-1.94
27	10							77.0	0.0722	1.0690	0.0558	8.70	8.42	0.28
28	5.3						12.84	77.0	0.1932	1.0551	0.0390	4.20	7.40	-3.20
29		5						77.0	0.1316	1.0291	0.0257	1.61	1.62	-0.01
30	10			30				77.0	0.1559	1.1494	0.1084	27.29	26.61	0.68
31	10					10		77.0	0.1005	1.0765	0.0691	13.01	18.04	-5.03
32	Field mud - unknown composition							59.9	0.0450	1.1750	0.1066	26.67	28.92	-2.25
* Hydrate temperature suppression data from reference 1											Absolute average deviat		1.40	

Table 2- Hydrate equilibrium conditions of the aqueous solutions tested in this work.

no.	Solution	Temp. [°F]	Pressure [psi]	no.	Solution	Temp. [°F]	Pressure [psi]
				19	10wt% KCl	75.3	5105
						77.0	5833
						71.4	3780
0	De-ionized water	82.9	5807			67.8	1742
		80.4	4215			62.9	1400
		80.6	4163				
		78.2	3203	20	5wt% KCl	76.8	5520
2	10wt% NaCl	73.5	5020		+ 10wt% glycerol	72.5	3937
		71.5	4070			71.3	2647
		66.4	2664			67.1	1406
		69.0	2308	25	10wt% NaCl	66.9	4044
3	5wt% NaCl -	80.5	6400		+ 10wt% glycerol	65.7	3104
		75.8	3875			62.7	2380
		77.9	4900			63.3	2392
4	5wt% NaCl	77.3	4960	28	5.34wt% NaCl	75.3	4260
	+ 5wt% glycerol	75.2	4095		+ 12.84wt% AquaCols	71.2	3257
		72.0	3080			67.6	2290
		71.0	2180	29	5wt% KCl	81.9	6000
10	10wt% NaCl	60.3	3770			79.4	4350
	+ 20wt% glycerol	60.0	3970			75.0	2965
		56.2	2352			76.5	3605
11	5wt% CaCl ₂	81.0	6320	30	10wt% NaCl	49.8	3420
		76.8	3695		+ 30wt% glycerol	49.2	2710
		75.8	2935			48.2	2020
13	5wt% CaCl ₂	75.2	5045			47.0	1365
	+ 20wt% glycerol	71.9	4030	31	10wt% NaCl+	61.0	3630
		69.4	3075		10wt% Propylene glycol	59.6	2865
		66.7	2160			57.0	2287
17	5wt%NaCl	77.3	4960	32	Unknown	50.0	3526
	+ 5wt% glycerol	75.2	4095			48.0	2910
		72.0	3080			46.2	2118
		71.0	2180			42.4	1524

Fig 1

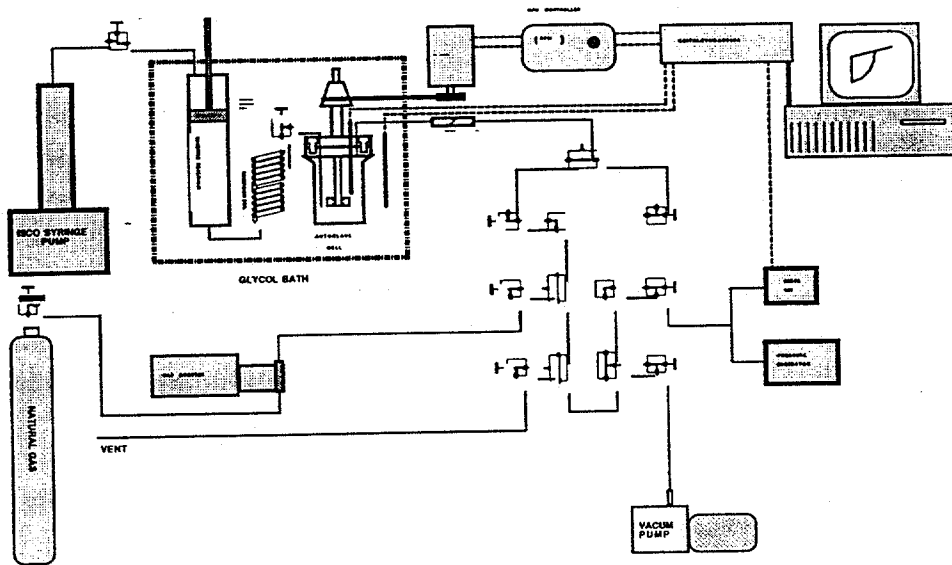
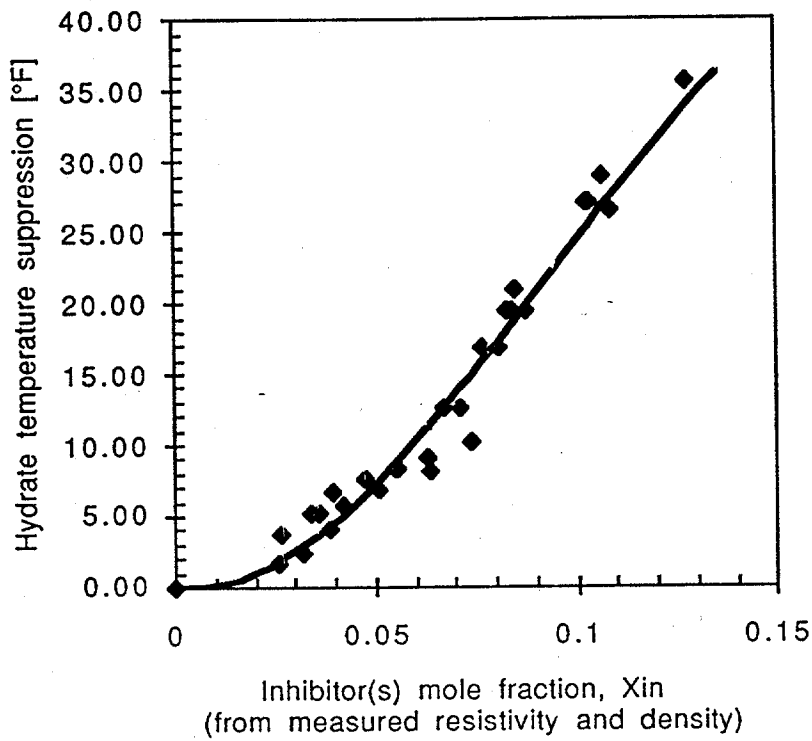


FIG. 1- HYDRATE TESTING DEVICE FOR DRILLING FLUIDS.

Figure 2- Hydrate temperature suppression of salts/glycols solutions.



5.0 Conclusions

1. We developed a model to predict the hydrate temperature suppression for drilling fluids.
2. The model predicts the hydrate temperature suppression using measured resistivity and density of the mud filtrate. These measurements can be performed on-site to provide real time hydrate prediction for the drilling fluid.
3. The model can also predict the hydrate suppression using the composition of the drilling fluids.
4. The model minimizes the need for costly experimental measurements.
5. The accuracy of the model is within the experimental error of the data used in obtaining the correlation parameters.
6. The model can be incorporated into a hydrate prediction model to determine the hydrate equilibrium pressure and temperature. (phase 2 of this project)

6.0 Nomenclature

a_w	Water activity, dimensionless
R	Universal gas constant, J/moleK
T	Equilibrium temperature, inhibited system, °F
T_0	Equilibrium temperature, water, °F
ΔT	Hydrate temperature suppression, °F
a_1, a_2, a_3	Polynomial coefficients of Equation (3), °F
x_{in}	mole fraction, mol/mol
α	Degree of ionization, dimensionless
w_j	weight %, component j : salt, glycol or water, g/100g
M_j	Molecular weight, component j : salt (s), glycol (a) or water (w), mol/g
ϵ	Mixture coefficient, Equation (A13), mole/100g
C	Factor of Equation (6), 100g/cc
ρ_{mix}	Filtrate density, kg/liter
ρ_j	Fluid component density, j : glycol (a) or water (w), kg/liter
R_{mix}	Filtrate resistivity, ohm-m
R_w	Resistivity of NaCl in water, ohm-m
β_1, β_2	Resistivity correction factor, dimensionless

7.0 References

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APPENDIX A

Hydrate temperature suppression

Gibbs-Duhem equation expresses the phase equilibrium of a binary system (solid-liquid) as the following relationship⁵:

$$\ln a_w = -\frac{\Delta h}{RT} \left(1 - \frac{T}{T_0}\right) + \frac{\Delta C_p}{R} \left(\frac{T_0 - T}{T}\right) - \frac{\Delta C_p}{R} \ln \left(\frac{T_0}{T}\right) \quad (\text{A1})$$

Where a_w is the water activity, T is the hydrate equilibrium temperature of the inhibited solution, T_0 is the hydrate equilibrium temperature of uninhibited system.

The difference between fluid and hydrate enthalpy, Δh and heat capacity, ΔC_p are assumed constant within the range of calculation. R is the universal gas constant. Equation A1 can be rewritten in the following form after neglecting the second and third terms on the right hand side:

$$\ln a_w = -\frac{\Delta h}{RT} \left(1 - \frac{T}{T_0}\right) \quad (\text{A2})$$

Activity is usually split into two terms, water concentration x_w and activity coefficient γ_w . The simplest expression, Margules equation, gives water activity as a function of inhibitor fraction x_{in} and temperature T .

$$x_{in} = 1 - x_w$$

$$\ln a_w = \ln x_w + \ln \gamma_w$$

$$\ln a_w \approx \ln(1 - x_{in}) - \frac{A}{RT} x_{in}^2 \quad (\text{A3})$$

Where A is a constant. The gas hydrate temperature suppression, ΔT is the difference between the hydrate equilibrium temperature of the inhibited system and pure water.

$$\Delta T = T_0 - T \quad (A4)$$

Combining equations A2, A3, and A4:

$$\Delta T \approx \frac{\frac{A}{R} x_{in}^2 - T_0 \ln(1 - x_{in})}{\frac{\Delta h}{RT_0} - \ln(1 - x_{in})}$$

$$\Delta T \approx \frac{\frac{A}{R} x_{in}^2 + T_0 \left(x_{in} + \frac{x_{in}^2}{2} + \frac{x_{in}^3}{3} + \dots \right)}{\frac{\Delta h}{RT_0} + \left(x_{in} + \frac{x_{in}^2}{2} + \frac{x_{in}^3}{3} + \dots \right)}$$

By neglecting higher order terms, the hydrate temperature suppression, ΔT can be represented as a third degree polynomial in terms of the inhibitor(s) mole fraction, x_{in} :

$$\Delta T = a_1 x_{in} + a_2 x_{in}^2 + a_3 x_{in}^3 \quad (A5)$$

Inhibitor fraction

The method of Zdanovskii, Stokes and Robinson⁷ is simplified and combined with Hammerschmidt's² equation of inhibitor fraction in a binary systems to derive the equation of inhibitor fraction, x_{in} in ternary system.

The solute is considered a ternary system of water (w), salt (s) and glycol (a). Water activity is predicted by using data of binary solutions which, at isobaric equilibrium, have the same water activity as the ternary solution. Zdanovskii et al.'s method⁷ is based on an empirical relationship between the molalities, m , of the solutes.

$$a_w = a_{w,s}^0 = a_{w,a}^0$$

$$1 = \frac{m_s}{m_s^0} + \frac{m_a}{m_a^0} + \left(b \frac{m_s m_a}{m_w} \right) \quad (\text{A6})$$

m_s and m_a refer to molality [mol/kg water] of salt and glycol respectively in the ternary solution, and m_s^0 , m_a^0 are the molalities in binary solutions with same water activity as the ternary solution.

Definition of salt molality in binary solution:

$$m_s^0 = \frac{10^3}{M_s} \frac{w_s^0}{(100 - w_s^0)} \quad (\text{A7})$$

Hammerschmidt's equation for salt molefraction in binary solution is:

$$x_{0s} = \frac{(\alpha + 1) \frac{w_s^0}{M_s}}{\left(\frac{w_s^0}{M_s} + \frac{(100 - w_s^0)}{M_w} \right)} \quad (\text{A8})$$

Combining (A7) and (A8), the molality of salt in water can be expressed as a function of Hammerschmidt's mole fraction :

$$\frac{1}{m_s^0} = \frac{M_w}{10^3} \left(\frac{(\alpha + 1)}{x_{0s}} - 1 \right) \quad (\text{A9})$$

The same approach can be used to express molality of pure glycol solved in water :

$$\frac{1}{m_a^0} = \frac{M_w}{10^3} \left(\frac{1}{x_{0a}} - 1 \right) \quad (\text{A10})$$

Our model assumes that water activity can be replaced with the inhibitor mole fraction, with reference to Margules equation (A3). The boundary of equal water activity in (A6) is thereby simplified to equal inhibitor mole fractions.

$$x_{in} = x_{0s} = x_{0g} \quad (A11)$$

Combining (A6), (A9), (A10) and (A11) to replace the inhibitor molalities of the binary solutions in the relationship between the molalities, and solving for x_{in} :

$$1 = \frac{M_w}{10^3} \left(\frac{(\alpha + 1)}{x_{in}} - 1 \right) m_s + \frac{M_w}{10^3} \left(\frac{1}{x_{in}} - 1 \right) m_g + \left(b \frac{m_s m_a}{m_w} \right)$$

$$x_{in} = \frac{(\alpha + 1)m_s + m_a}{m_s + m_a + \frac{10^3}{M_w} \left(1 - b \frac{m_s m_a}{m_w} \right)}$$

As the degree of ionization in mixture equals that of a binary solutions of salt in water with same inhibitor fraction as the ternary solution, x_{0s} .

Inhibitor fraction expressed in terms of mole fraction:

$$x = \frac{(\alpha + 1) \frac{w_s}{M_s} + \frac{w_a}{M_a}}{\frac{w_s}{M_s} + \frac{w_a}{M_a} + \frac{w_w}{M_w} - \epsilon} \quad (A12)$$

$$\epsilon = \frac{10^6 b}{w_w} \left(\frac{w_s w_a}{M_s M_a} \right)$$

For most mixtures an average value of the correction factor b is found empirically, or Correa and Vega propose a power series of water activity or ionic strength (only valid for mixed salt).

An average value of b is not sufficient for the highly inhibited systems, and using water activity would complicate the calculations. We chose to fit the mixture coefficient ϵ to experimental data of inhibitor fraction in ternary systems, published by Yousif and Young¹.

$$\epsilon = \frac{62.203M_w}{w_w} \left(\frac{w_s w_a}{M_s M_a} \right) - 10.06 \left(\frac{100 - 3.49w_s}{w_w} \right) \sqrt{\frac{w_s w_a}{M_s M_a}} \quad (\text{A13})$$

This mixture coefficient ϵ is unit consistent, and the mixture inhibitor fraction x_{in} converges to Hammerschmidt's² equation for a binary system of either inhibitor in water, as ϵ approaches zero.

APPENDIX B

Mathematical development for calculating hydrate temperature suppression in mixed solution from measured resistivity and density data.

Step 1: Determine the weight fractions of salts, w_s and glycol, w_a

Use the logarithm of Equation 6 to define a function ϕ that approaches zero as w_s and w_a approach the equivalent inhibitor fractions:

$$\phi = \ln(R_w) - \ln(R_{mix}) + \left(0.94126 * 10^{-3} \beta_1 + \frac{6.38052}{(1 + \beta_2)} + \frac{8.79405}{(1 + \beta_2)^2} \right) \quad (\text{B1})$$

$$\beta_1 = \frac{\rho_{mix} w_a}{\rho_a - \rho_w} \quad \text{and} \quad \beta_2 = \frac{M_a}{M_w} \left(\frac{(100 - w_s)}{w_a} - 1 \right) \quad (6)$$

In Equation B1, the NaCl equivalent solution resistivity, R_w is calculated by a polynomial expression which was developed from literature data⁶:

$$\ln(R_w) = \sum_{j=0}^7 \left(\sum_{k=0}^4 (A_{jk} T_m^k) z_w^j \right), \text{ where } z_w = \ln \left(\frac{w_s}{1.241809913} \right) \quad (\text{B2})$$

w_s is the NaCl weight % in solution, valid in the range 0.5-26 wt%. T_m is the temperature, valid in the range 32-212 °F. The polynomial coefficients, A_{jk} are given in Table B1.

Table B1

A _{jk}	k = 0	1	2	3	4
j = 0	4.74104E-01	-2.35959E-02	1.29709E-04	-4.83933E-07	7.55467E-10
1	-9.62353E-01	4.16177E-04	-1.37509E-07	-1.00850E-08	
2	-1.20604E-02	2.63410E-04	-7.95574E-07		
3	5.93768E-03	7.70651E-05			
4	3.50966E-03	-1.03747E-05			
5	-1.29672E-03	-7.36658E-06			
7	1.57024E-04				

By substituting Equation 7m and 8 for w_a and C respectively, ϕ is made a function of w_s only.

$$C = C_1 + C_2 w_s \quad (8)$$

$$C = 7.80979 * 10^{-3} - 1.566 * 10^{-5} T_m + 5.657 * 10^{-8} T_m^2 + 2.418 * 10^{-5} w_s$$

$$w_a = \left(\frac{100 - w_s}{1 - \rho_w / \rho_a} \right) \left(1 - \frac{\rho_w}{\rho_{mix} - C w_s} \right) \quad (7m)$$

For a numerical approximation, we calculate the 1. order derivative of ϕ to w_s and use an iterative procedure to calculate w_s :

$$\frac{\partial w_a}{\partial w_s} = -w_a \left[\frac{1}{100 - w_s} + \frac{C_1 + 2C_2 w_s}{\left(\frac{\rho_{mix} - C w_s}{\rho_w} - 1 \right) (\rho_{mix} - C w_s)} \right] \quad (B3)$$

$$\frac{\partial \beta_2}{\partial w_s} = \frac{-M_a}{M_w w_a} \left(1 + \frac{(100 - w_s)}{w_a} \frac{\partial w_a}{\partial w_s} \right) \quad (B4)$$

$$\frac{\partial \ln(R_w)}{\partial w_s} = \frac{1}{w_s} \sum_{j=1}^7 \left(\sum_{k=0}^4 j (A_{jk} T_m^k) z_w^{j-1} \right) \quad (B5)$$

$$\frac{\partial \phi}{\partial w_s} = \frac{\partial \ln(R_w)}{\partial w_s} + 0.94126 * 10^{-3} \frac{\beta_1}{w_a} \left(\frac{\partial w_a}{\partial w_s} \right) - \left(\frac{6.38052}{(1+\beta_2)^2} + \frac{17.58810}{(1+\beta_2)^3} \right) \left(\frac{\partial \beta_2}{\partial w_s} \right) \quad (\text{B6})$$

Iterate:

$$w_s^{**} = w_s^* - \frac{\phi^*}{\left(\frac{\partial \phi}{\partial w_s} \right)^*}$$

Stopcriterion:

$$\begin{aligned} |w_s^{**} - w_s^*| &\leq \delta \\ \delta &= 10^{-4} \end{aligned} \quad (\text{B7})$$

Choose a start value w_s^* , and solve Eqs. B1 through B7. Iterate until the stop criterion is reached.

Step 2: Determine the total mole fraction of the inhibitors, x_{in} and the hydrate temperature suppression, ΔT

Define K1 and K2 as inhibitor dependent constants, calculated from values found in step 1 by using Equation 4 :

$$K_1 = \frac{w_s}{M_s} + \frac{w_a}{M_a} \quad \text{and} \quad K_2 = \frac{w_w}{M_w} - \varepsilon \quad (\text{B8})$$

The degree of ionization is found by solving Eqs. B9 and B10 simultaneously for α and w_{s0} . Equation B9 is a fit from tabulated data⁸ of NaCl in water at 68 °F. Equation B9 was obtained from combining Eqs. 3m and A8.

$$\begin{aligned} \alpha = & 0.8088 - 0.05379 \ln(w_{s0}) + 0.002280 \ln(w_{s0})^2 \\ & - 0.001946 \ln(w_{s0})^3 - 0.001960 \ln(w_{s0})^4 \end{aligned} \quad (\text{B9})$$

$$w_{s0} = 100 \left(1 + \frac{M_w}{M_s} \left(\frac{K_2 + \alpha \left(K_2 + \frac{w_a}{M_a} \right)}{K_1 + \alpha \frac{w_s}{M_s}} \right) \right)^{-1} \quad (\text{B10})$$

Rearrange Equation 3 using Equation B8 to calculate the inhibitor(s) mole fraction :

$$x_{in} = \frac{\frac{\alpha w_s}{M_s} + K_1}{K_1 + K_2}$$

Finally, the hydrate temperature suppression is calculated from Equation 11:

$$\Delta T = -38.552x_{in} + 4350.4x_{in}^2 - 15420x_{in}^3 \quad (11)$$

Example Calculation

Input data :

measurement temperature, T_m	77.0 [$^{\circ}$ F]	glycol density, ρ_a	1.2777 kg/liter]
measured filtrate resistivity, R_{mix}	0.112 [ohm-m]	glycol molecular weight, M_a	92.11 [kg/kmol]
measured filtrate density, ρ_{mix}	1.121 [kg/liter]		

Step 1:

Guess a start value for the salt concentration. Calculate B1 through B6, to receive an improved value. Repeat calculation using the new value of w_s , until criterion is reached.

Calculated values from each iteration are shown below :

	(B4)	(7m)	(B1)	(B3)	
Iterations:	w_s	w_a	ϕ	$\delta\phi$	$-\phi / \delta\phi$
start	5.0000	35.3080	1.04762	-0.27258	3.8434
1	8.8434	23.8052	0.22992	-0.16972	1.3547
2	10.1981	19.7637	0.01426	-0.14953	0.0954
3	10.2935	19.4794	6.5524E-5	-0.14827	0.0004
4	10.2939	19.4781	7.5468E-9	-0.14826	0.0000
5	10.2939	19.4781			

The properties correspond to a mixed solution of 10.2939 wt% NaCl and 19.4781 wt% glycerol.

Step 2:

$$K_1 = 0.38758 \quad \text{and} \quad K_2 = 5.07425$$

The degree of ionization is found by solving Eqs. B8 and B9 simultaneously. Input the values of K_1 and K_2 .

$$\alpha = 0.8088 - 0.05379 \ln(w_{s0}) + 0.002280 \ln(w_{s0})^2 - 0.001946 \ln(w_{s0})^3 - 0.001960 \ln(w_{s0})^4$$

$$w_{s0} = \frac{38.758 + 17.115\alpha}{1.95153 + 1.80524\alpha}$$

Start the iterations at :	w_{s0}	α
$w_{s0}^* = w_s + w_a / 3 =$	16.78665	0.50749
	16.63225	0.50992
	16.62178	0.51008
	16.62107	0.51009
	16.62107	0.51009

Total inhibitor mole fraction, x_{in} and hydrate temperature suppression, ΔT :

$$x_{in} = \frac{\frac{\alpha w_s}{M_s} + K_1}{K_1 + K_2} = 0.0874$$

$$\Delta T = -38.552x_{in} + 4350.4x_{in}^2 - 15420x_{in}^3 = 19.57^\circ F \quad (11)$$

The measured values correspond to sample 10, of 10 wt% NaCl and 20 wt% glycerol. The hydrate temperature suppression was measured to 19.58 °F.