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EFFECTS OF SOLUTES AND THIRD SURFACES ON VAPOR PRESSURE OF AQUEOUS SYSTEMS

by

Abdelhamid Ouar

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillement of the requirements for the degree of Master of Science in Applied Chemistry.

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ABSTRACT

The main objective of the present work was to evaluate the effects of the addition of salts and third surfaces on the vapor pressure of aqueous systems. Vapor pressure measurements were carried out in five different aqueous systems and surface tension measurements were performed on four of these test fluids. Results indicated that the vapor pressure of the solvent (water) is lowered in the presence of salts, while it was, surprisingly, increased in the presence of the third surfaces investigated. The surface tension increased when the vapor pressure was lowered, and decreased when the vapor pressure increased. The magnitude of the changes were more pronounced in the surface tension measurements in the presence of third surfaces. The results of this study show that both vapor pressure and surface tension are good indicators of the potential of gas hydrate formation of aqueous systems. The limitations of both methods are discussed. Another finding of this work, is that the mechanism of inhibition of gas hydrate formation can be attributed to an ordering (entropy) effect, while an energetic (enthalpy) effect is responsible for the promotion.

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To All My Friends in America

INTRODUCTION

Natural gas hydrates are non-stoichiometric solid inclusion compounds formed when natural gas comes into contact with water at lower temperatures and elevated pressures (1,2). A combination of considerable strength occurs when the size and shape of the guest molecule optimally fits within the cavity formed by the host molecules. The water molecules form a lattice structure through hydrogen bonding, but the water cages only interact with the gas molecules through van der Waals forces. In the case of natural gas hydrates, the gas molecules are the guest species and the water molecules form the host lattice(3,4,5).

Recently, the oil industry has been facing an increasing danger of hydrate formation during drilling operations as the industry has been extending its efforts to deeper waters, where the conditions of pressure and temperature are very favorable to hydrate formation. Consequently, the oil industry has been greatly concerned with the problem of hydrate formation and the potential safety danger and economical problem it does present (6,7,8). Recent work, in our laboratory, on hydrate formation in drilling muds, has shown thermodynamic and kinetic enhancement of hydrate formation as compared to pure water (9,10,11). Further investigation has shown that this promotion of the hydrate formation could be attributed to the addition of a third surface to the gas-water system (11,12). However, the oil industry is more concerned with the prevention or at least the inhibition of hydrate formation. Therefore, most research efforts have been focused on developing inhibitive methods of hydrate formation (13,14). Two main approaches to predicting hydrate formation have been considered.

The first approach is to investigate hydrate formation in different drilling fluids to determine the effects of their individual components on hydrate formation. The objective of this approach was to use the data to formulate drilling fluids highly inhibitive to hydrate formation. The hydrate formation experiments are conducted at relatively high pressures (2 to 20 MPa) and typically require between 40 to 70 hours per run. From a more fundamental aspect, the effects of the addition of a third surface or an inhibitor on the formation variables of natural gas hydrate , can be explained by a change in the activity of the water present in the system.

A second alternative to evaluate the hydrate formation potential of a given fluid is to calculate its activity. The experimental determination of the activity of a given fluid is generally accomplished through the measurement of one of its colligative properties (15). Nielsen and Bucklin (16) , who studied natural gas hydrate inhibition in pipelines, have developed a quantitative relation between water freezing point depression and hydrate point depression. Hale and Dewan (14) refined this relation and calculated the activities of the different fluids they studied through the measurement of their freezing point depression. They, then predicted the hydrate formation conditions in these fluids by using the calculated activities in a predictive model CSMHYD developed at the Colorado School of Mines (17,18). Colligative properties experiments are simpler, more economical and require much less time than a typical high pressure hydrate formation experiment. If accurate, they provide an easy method of evaluation of the potential for hydrate formation of a given fluid.

Initially, attempts were made to carry out freezing point depression measurements in a Differential Scanning Calorimeter, Perkin-Elmer DSC-2. However, this analytical method presented two major limitations; first, the small sample size of 100 l generated doubts on how representative is the sample; second, the metastability associated with any freezing point measurement posed a problem.

Consequently, it was decided to measure a different colligative property, vapor pressure lowering, to evaluate the activity of the different fluids tested. Vapor pressure measurements present certain advantages since a representative sample can be used, and since there is no metastability associated with the measurement. The vapor pressure is a strong function of temperature, and its measurement over a range of temperatures will allow a better evaluation of the activity than if calculated from a single freezing point measurement at one given temperature. The vapor pressure measurements will also provide the heat of vaporization of the fluid and this could, eventually, be correlated to the heat of hydrate dissociation.

The present paper will address the effects of the addition of a third surface or an inhibitor on the vapor-pressure of a given fluid and how it can be translated to the prediction of hydrate formation promotion or inhibition.

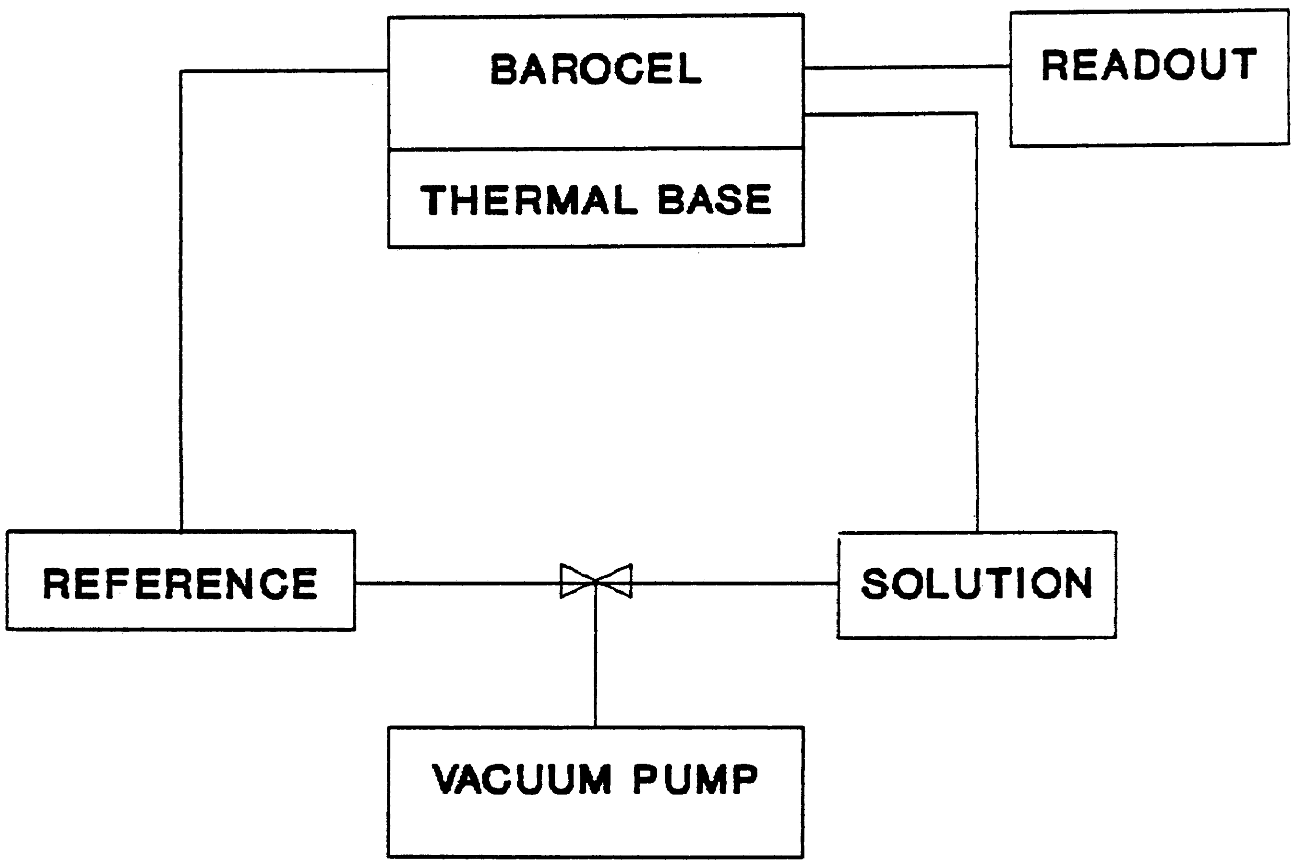
EQUIPMENT AND REAGENTS

The experimental apparatus is described in Figure 1. The heart of the system is a Datametrics Barocel pressure sensor, type 570, with a pressure range 0-2000 Torr, capable of measuring down to 0.0001 Torr. The pressure sensing element is a high precision stable capacitive potentiometer with a thin, highly prestressed metal diaphragm. Positioned between fixed capacitor plates, the diaphragm forms the separation between two gas-tight enclosures which are connected to the external ports. A difference in total pressure within the enclosures produces a force which deflects the diaphragm and varies the relative capacitance of the diaphragm and the fixed capacitor plates. The voltage output versus pressure input of the pressure sensor is perfectly linear. The transducer is mounted on a thermal base which acts as a large heat source that minimizes the effects of temperature transients and avoids any vapor condensation in the barocel. The barocel is connected to an Electronic Manometer readout which gives a digital pressure reading with an accuracy of .15 to 0.05% of reading.

A typical experimental set-up consists of connecting one port of the transducer to the sample solution and the second port to a reference. The experiments were performed

Figure 1

Experimental Apparatus



in a large, well-mixed, water bath. The bath temperature was controlled through balancing an immersed heater against a refrigeration unit. The temperature of the bath was monitored by an Omega RTD probe accurate to +/- 0.15 K. Vacuum and water were used as pressure references in the experiments. When water was the reference, the water flask was immersed in the same bath as the sample, so its vapor pressure at the bath temperature was the pressure reference.

The vapor pressure of the following fluids were measured: water, sodium chloride solutions, sodium bromide solutions, bentonite (sodium montmorillonite from Wyoming) gel, and a drilling fluid containing bentonite, chrome-lignosulfonate, reagent-grade NaOH, drill solids, and partially (30%) hydrolyzed polyacrylamide (PHPA). The water used was deionized while all the chemicals used in the different fluids were reagent grade.

Sodium chloride and sodium bromide are known hydrate inhibitors (19,20) while hydrate promotion has been observed in the bentonite gel and the drilling fluid studied (11,12). Consequently, the study of these five fluids should provide insight into to both hydrate promotion and inhibition mechanisms.

EXPERIMENTAL PROCEDURE

When vacuum was used as pressure reference, a sample solution of approximately 100 ml was loaded in a 250 ml glass flask. The flask was connected to the barocel via a flexible stainless steel tubing with a heating tape around it to avoid any vapor condensation during the measurement. Both the flask and the tubing are evacuated to ensure that the vapor pressure measured is that of the fluid studied. A more detailed of the degassing procedure is described in Appendix H. After zeroing of the electronic manometer, the flask is opened to the barocel and the vapor pressure of the sample is measured.

The measurements were done over a range of temperatures between 288 and 320 K; at each temperature step, 30 minutes were allowed for equilibrium before a reading of the vapor pressure was taken. For each fluid, the measurement was performed twice as the temperature was increased and then decreased over the range studied. When water vapor pressure was used as pressure reference, 100 ml of water were loaded in a 250 ml glass flask and connected to the opposite side of the barocel via a flexible stainless stell tubing with heating tape. Both flask and tubing were evacuated prior to any measurement. The electronic manometer readout was zeroed by connecting both sides of the barocel to the vacuum while the valves are closed to the flasks. Prior to any relative measurement, the standard (water) vapor pressure is measured against vacuum.

RESULTS AND DISCUSSION

Our initial experimental effort consisted of measuring the vapor pressure of pure water and sodium chloride solutions, at different concentrations, against vacuum. The results of these measurements were compared to available literature values to validate our experimental method. These results, summarized in Table 1, show good agreement with the literature values. The average relative error is always less than +/- 2%. This average relative error (21) is calculated as:

Sum (experimental value-true value/true value)/sum number of readings.

A second order polynomial fit of the vapor pressure as function of absolute temperature and wt% NaCl was developed from literature data (22):

$$\ln P = 17.88684 - 3490.72896 * 1/T - .113917*10^{-2}*X$$
$$-.267309*10^{6}*(1/T)^2 - 1.116349*(1/T)*X - .287865*10^{-3}*X^2$$

where P is in Torr, T in degree Kelvin and X is weight% NaCl. Also, the error analysis does not show any positive nor negative systematic error. No hysteresis was recorded as the temperature was decreased and then increased during the measurements. Figure 2 illustrates the agreement between the experimental data and the literature data for two of the test fluids, water and 20 wt% NaCl solution. The addition of sodium chloride to water resulted in the lowering of the vapor pressure of the solution, indicating a decrease of the activity of the water. Note that the vapor pressure lowering is proportional to the salt concentration in the aqueous solution.

Since an objective of this work was to evaluate the effects of the addition of inhibitors and third surfaces on the activity of pure water, it was decided to perform all the subsequent tests using water as reference. Also, the computer hydrate formation prediction model is very sensitive to the activity, requiring its knowledge to three significant digits. Table 2 presents the results of the vapor pressure measurements of three different sodium chloride solutions with respect to water. This relative measurement extended the barocel range by one order of magnitude allowing a reading with one more significant digit than in the absolute measurement (against vacuum). The

Figure 2

Comparison of Experimental and Literature Data

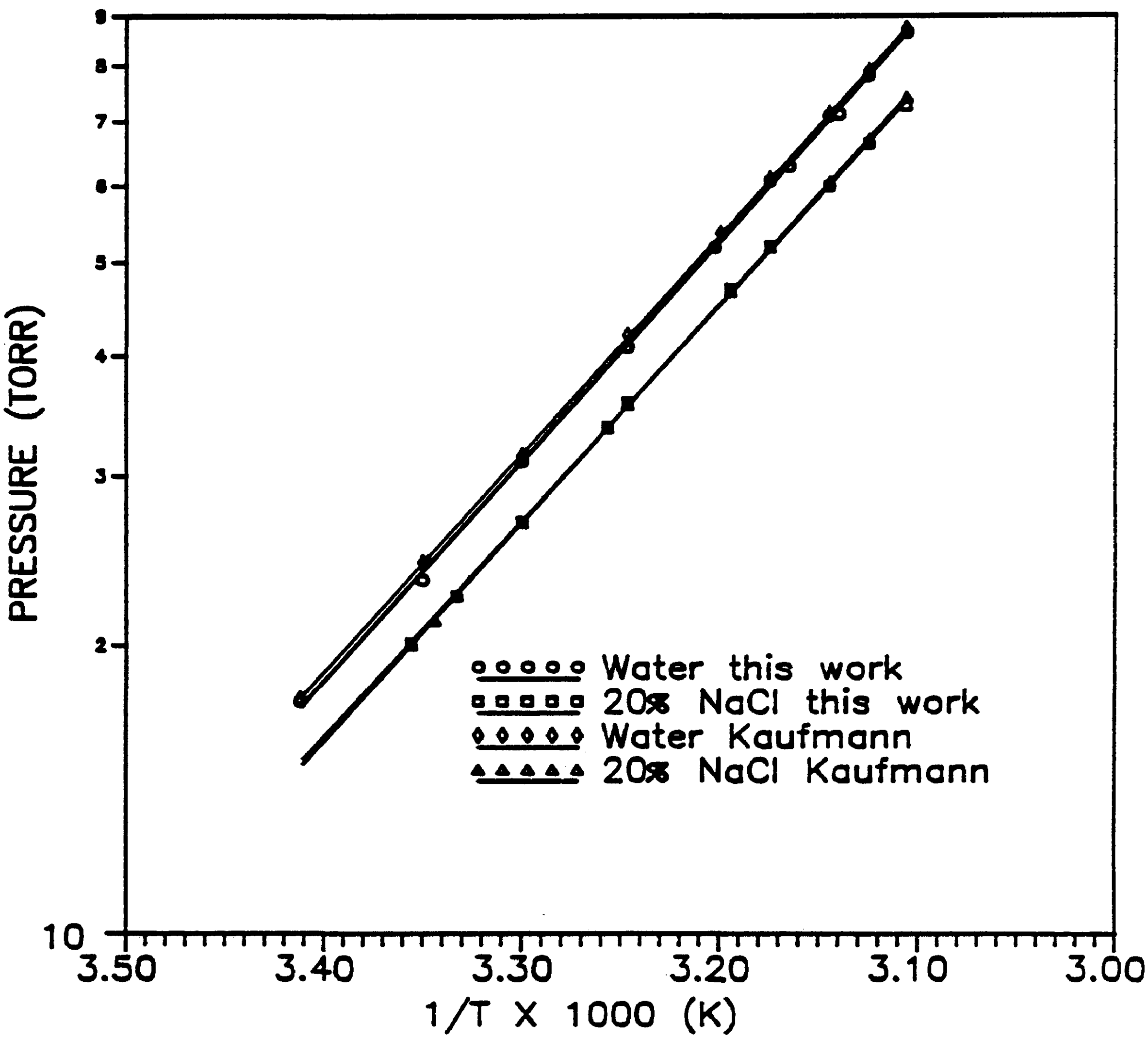


Table 1:Vapor Pressure Measurement of Water and NaCL Solutions versus Vacuum

	Water			20%Nacl		
T(K)	Exp P(Torr)	Lit P(Torr)	%Err.	Exp P(Torr)	Lit P(Torr)	%Err.
322.0	86.48	87.18	-0.8	72.60	74.16	-2.1
320.0	78.12	78.87	-0.9	66.36	67.07	-1.0
318.0	70.90	71.26	-0.5	59.96	60.57	-1.0
315.0	60.74	61.02	-0.5	52.00	51.83	0.3
313.0				46.94	46.62	0.7
312.5	51.80	53.48	-3.1			
308.0	40.80	41.91	-2.6	35.72	35.54	0.5
303.0	31.06	31.45	-1.2	26.88	26.81	0.3
299.0				21.12	21.22	-0.5
298.5	23.38	24.35	-3.9			
293.1	17.45	17.56	-0.6			
		Avg:	-1.6			Avg:-0.4

	15% NaCl			10% NaCl		
T(K)	Exp P(Torr)	Lit P(Torr)	%Err.	Exp P(Torr)	Lit P(Torr)	%Err.
321.0	72.06	75.06	-3.9			
320.0	70.00	71.37	-1.9			
319.0	66.60	67.84	-1.8	69.80	71.16	-1.9
318.0	63.70	64.46	-1.1			
317.0				64.04	64.22	-0.3
316.0				61.84	60.98	1.4
312.0	46.28	47.05	-1.6			
308.0	37.50	37.84	-0.9	39.76	39.72	0.1
304.0				31.98	31.74	0.8
303.0				30.22	29.98	1.0
302.0	26.36	26.95	-2.2	29.58	28.30	1.0
298.0				22.75	22.38	1.6
			Avg:-1.9			Avg:0.5

results presented in Table 2, show that the average relative error in the measurement against water can be translated to an average relative error of one order of magnitude less when the experimental difference is used to evaluate the experimental vapor pressure of the solution. The %Err.A is the relative error recorded in the measurement with water as reference:

%Err.A = (Experimental difference - True difference)/true difference)) x 100

while %Err.B is defined as:

%Err.B =((Pwater - experimental difference)-PNaCl))/PNaCl x 100

This improvement in the accuracy of the vapor pressure measurement is important since it means an evaluation of the activity with a better accuracy (a gain of one significant digit).

Colligative properties of solutions depend only on the number, but not the kind of solute particles in a given amount of solvent. Therefore, the same relative measurements were performed on sodium bromide solutions that were equimolal to the sodium chloride solutions used. As expected the vapor pressure measurements of the NaCl and NaBr solutions, for the same molality were very close as shown in Figure 3. The results of these runs are summarized

Table 2: Relative Vapor Pressure Measurements of Sodium Chloride Solutions

5% NaCl				10% NaCl			
T(K)	EXP ΔP(Torr)	%Err.A	%Err.B	T(K)	EXP ΔP(Torr)	%Err.A	%Err.B
315.2	1.6202	38.1	-0.7	320.0	4.804	19.6	-1.0
303.3	0.6648	4.9	-0.1	318.0	3.532	- 3.1	0.2
297.9	0.4802	2.2	-0.04	311.8	2.348	-12.0	0.7
292.7	0.2620	-40.3	0.5	310.7	2.920	15.8	-0.9
288.4	0.2492	- 7.5	0.2	306.8	2.274	10.7	-0.6
292.1	0.4410	31.0	-0.6	302.2	1.860	16.3	-0.9
296.9	0.5294	17.7	0.4	296.8	1.308	11.0	-0.6
302.7	0.6340	3.2	-0.06	292.0	1.068	20.4	-1.2
308.3	1.0728	29.7	-0.5	295.0	1.544	45.5	-2.6
311.5	1.3314	36.6	-0.7	305.8	2.720	39.8	-2.2
314.2	1.6236	45.4	-0.9	314.5	3.740	22.1	-1.2
			Avg.-0.3				Avg:-0.9

15% NaCl				20% NaCl			
T(K)	EXP ΔP(Torr)	%Err.A	%Err.B	T(K)	EXP ΔP(Torr)	%Err.A	%Err.B
299.0	2.452	- 0.7	0.08	312.7	8.968	9.2	-1.6
303.5	3.580	12.4	-1.4	303.0	5.680	17.4	-3.1
314.3	5.916	4.8	-0.5	298.0	4.458	22.1	-4.0
326.6	11.300	9.9	-1.0	292.2	3.286	27.9	-5.1
322.8	7.654	-10.9	1.1	301.5	4.568	2.7	-0.5
318.9	6.440	- 9.5	1.0	309.1	7.918	17.1	-3.0
313.7	5.340	- 2.5	0.3	310.7	8.610	17.0	-3.0
313.0	5.140	- 2.7	0.3	318.9	12.774	14.3	-2.5
308.3	4.060	- 7.1	0.2				
303.6	3.168	- 1.0	0.1				
299.9	2.586	- 0.5	-0.04				
297.7	2.284	- 0.4	-0.06				
292.8	1.726	0.6	-0.06				
288.0	1.260	- 1.4	0.2				
			Avg: 0.02				Avg:-2.8

in Table 3. The error analysis is the same as for sodium chloride and, similarly, a second order polynomial fit was developed from literature data (23):

$$\ln P = 18.46681 - 3831.38719 * 1/T - .000526 * X - 217461.85$$
$$* - 217461.85 * (1/T) + .019519 * (1/T) * X - .00019141 * X^2$$

As sodium chloride and sodium bromide were tested to study the effect of solutes on the vapor pressure (hence,the activity), bentonite and a drilling fluid were tested to evaluate the effect of a third surface on the vapor pressure of an aqueous system. Both bentonite and the drilling fluid are known to be thermodynamic promoters of gas hydrate formation. The results of these tests were very unusual as seen in Table 4. We actually did record an increase of the vapor pressure of the aqueous system due to the addition of the third surface. It is also interesting to note that the vapor pressure increase is more pronounced at low temperatures as was the thermodynamic promotion of gas hydrate formation (11). The magnitude of the increase in the vapor pressure varies between 1 to 10%. This increase was duplicated once for each fluid. The error analysis performed on the salt solutions suggests that this increase was real and not an artifact of the experimental method.

Figure 3

Vapor Pressure of Equimolal Solutions of

NaCl and NaBr Solutions

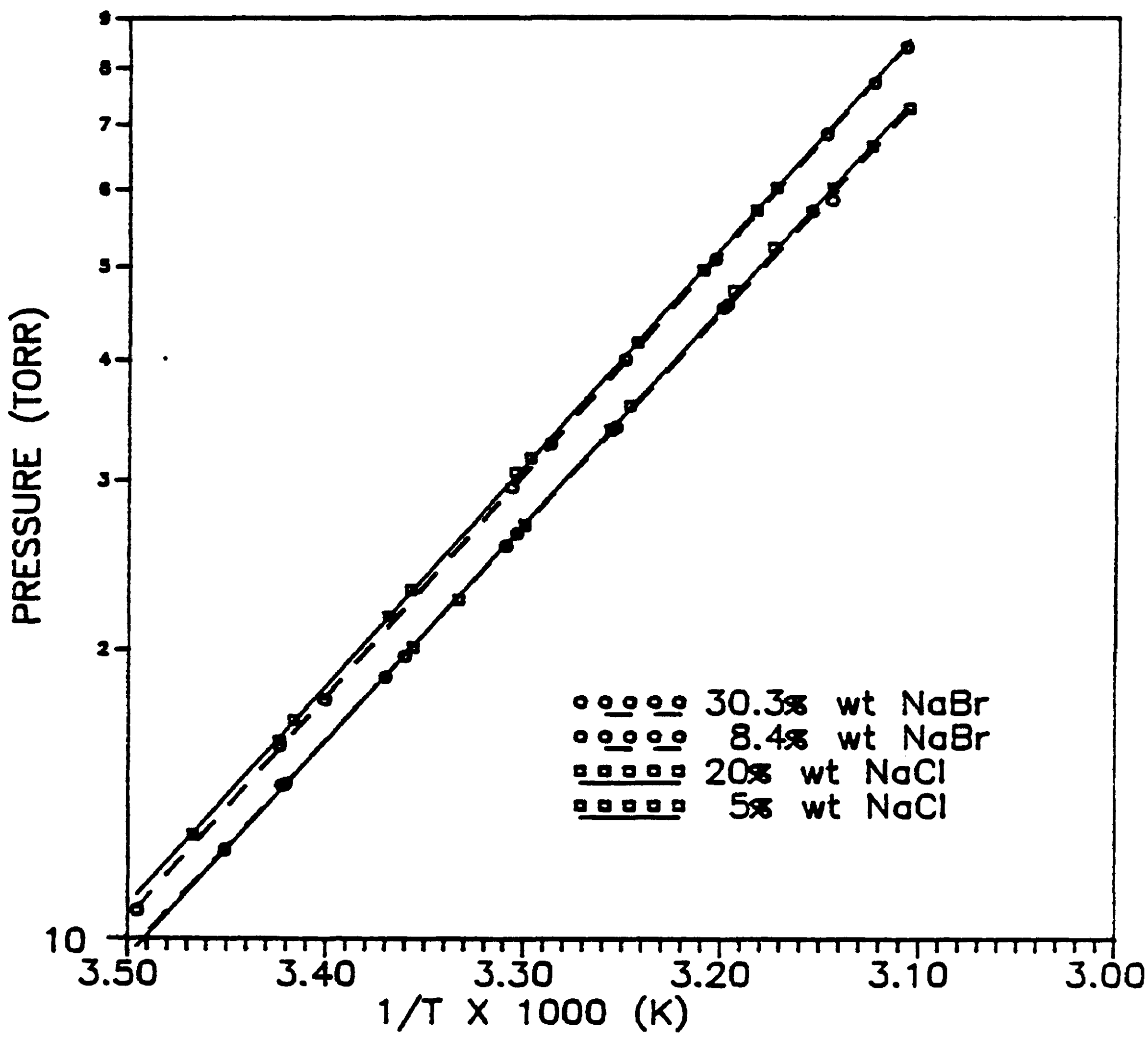


Table 3: Relative Vapor Pressure Measurements of Sodium Bromide Solutions

8.4%wt NaBr				16.1%wt NaBr			
T(K)	EXP ΔP(Torr)	%Err.A	%Err.B	T(K)	EXP ΔP(Torr)	%Err.A	%Err.B
321.8	2.392	90.0	-1.3	316.3	3.808	- 8.4	0.6
317.7	1.9906	80.6	-1.3	310.8	2.694	- 0.7	0.04
304.2	1.2646	102.3	-1.9	302.9	1.720	- 3.7	0.2
291.9	0.7086	126.4	-2.5	296.4	1.120	- 8.9	0.5
286.1	0.5540	161.3	-3.0	290.4	0.720	-15.3	0.9
294.1	0.9636	168.4	-3.3	297.7	1.342	0.1	-0.06
302.5	1.3320	151.3	-2.7	305.0	2.036	1.6	-0.1
307.8	1.5426	108.2	-2.0	308.0	2.400	3.3	-0.2
312.1	1.7088	91.4	-2.0	312.5	3.030	2.6	-0.2
320.1	2.214	34.7	-0.7	317.1	3.770	2.3	-0.2
			Avg:-2.1				Avg:0.2

20.7%wt NaBr				30.3%wt NaBr			
T(K)	EXP ΔP(Torr)	%Err.A	%Err.B	T(K)	EXP ΔP(TORR)	%Err.A	%Err.B
317.8	7.254	-40.0	8.3	317.8	12.292	1.6	-0.3
312.7	6.686	41.8	-4.0	312.7	8.724	- 7.6	1.6
307.1	3.932	11.8	-1.1	307.3	6.634	- 9.0	1.9
299.8	3.496	49.3	-4.8	302.7	4.778	-11.7	2.5
292.7	2.692	71.5	-7.4	296.7	3.172	-16.8	3.4
296.2	3.286	73.5	-7.2	292.4	2.320	-20.9	4.4
304.8	4.636	49.3	-4.8	289.8	1.916	-23.0	4.9
308.4	5.328	41.3	-4.0	292.2	2.166	-25.2	3.2
311.5	5.972	34.7	-3.3	297.6	3.408	-15.3	2.6
317.1	7.514	28.0	-2.6	302.2	4.624	-12.1	2.1
				312.5	8.392	-10.2	1.9
				317.0	10.826	- 9.1	1.4
			Avg:-4.4				Avg:2.3

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Table 4: Relative Vapor Pressure Measurements of Aqueous Systems in the Presence of Third surfaces

	Water	Mud 13		Water	Bentonite
T(K)	P(Torr)	P(Torr)	T(K)	P(Torr)	P(Torr)
313.9	57.60	59.08	317.8	70.53	72.89
307.5	40.77	42.35	310.2	47.26	49.59
302.7	31.11	32.71	303.0	31.65	33.91
297.5	22.94	24.55	298.1	23.78	26.01
291.4	15.79	17.40	294.0	18.56	20.80
300.2	26.92	28.45	288.2	12.89	15.09
303.9	33.32	34.84	293.9	18.45	20.63
307.9	41.68	43.17	305.0	35.46	37.68
314.3	58.82	60.29	308.3	42.61	44.84
			310.8	48.82	51.08
			316.2	64.95	67.22

Furthermore, the vapor pressure of water and the sample were individually measured against vacuum prior to the relative measurement, for some runs, and also confirmed our results. Table 4 shows that the increase in vapor pressure was greater in the bentonite gel than in the drilling fluid. These results tend to confirm those of Cha et al(11) who reported a higher hydrate thermodynamic promotion with bentonite than the drilling fluid in consideration. All the measurements performed showed a strong dependency of the vapor pressure upon the temperature. This relation is expressed mathematically through the Clausius-Clapeyron equation

$$d(\ln P)/d(1/T) = -\Delta H/R$$

where $d(\ln P)/d(1/T)$ represents the slope of best fit vapor/liquid equilibrium lines, ΔH the heat of vaporization ,and R the universal gas constant. The heat of vaporization was calculated for every test fluid. These results are summarized in Table 5. It should be noted that the addition of salt shifts the vapor/liquid equilibrium line for water but does not affect its slope. This is indicative of a change in the ordering (entropy) of the system but not in the energy (enthalpy) of the system. On the contrary, the addition of a third surface induces a change in the slope of the vapor-liquid equilibrium line of water indicating a

Table 5: Heat of Vaporization of Test Fluids

	EXP ΔH KJ/mole	LIT ΔH KJ/mole
Water	43.65	40.88
20% NaCl	43.05	40.8
15% NaCl	42.41	40.8
10% NaCl	42.82	40.8
5% NaCl	43.61	40.8
30.3% NaBr	42.55	
20.7% NaBr	45.48	
16.1% NaBr	44.81	
8.4% NaBr	44.21	
Mud 13	41.43	
Bentonite	40.91	

change in the energy of the system. Since the vapor pressure of the water in presence of third surfaces is elevated, less heat is required to vaporize it.

The unusual vapor pressure elevation recorded during this work led to the measurement of the surface tension of the test fluids. It is known that the addition of a salt as solute increases the surface tension of the solvent (water) as it lowers its vapor pressure (22). Therefore, it may be that an elevation of the vapor pressure will be translated into a decrease of the surface tension. The surface tension measurements were made in a Fisher surface tensiometer which was calibrated using water as a standard. The results reported are the averages of four measured values of surface tension. These results are summarized in Table 6. The measurement of the surface tensions of both the bentonite gel and the drilling fluid showed a decrease in the surface tension of the aqueous system. In fact, in the case of the bentonite gel, the decrease was as high as 50% of the value for pure water.

Table 6: Surface Tension Measurements at 20 C

	Surface Tension, dynes/cm		Literature
Water	72.88	(standard)	
20%wt NaCl	80.51		79.75
Bentonite Gel	33.94		
Mud	68.31		

CONCLUSIONS

The vapor pressure of different aqueous systems was measured during the course of this work. The results were consistent and reproducible. The surface tension of most of these aqueous systems was also measured while the heat of vaporization of each test fluid was calculated from the vapor pressure data.

The results of this study confirmed that the addition of a salt to water lowers the vapor pressure of the solution while, surprisingly, the addition of the third surfaces investigated increases the vapor pressure of the aqueous system. These results can be translated into, respectively, a decrease or an increase in the activity of the aqueous system as the vapor pressure is lowered or increased. Since salts are known to be inhibitive of gas hydrate formation, and since promotion of gas hydrate formation has been recorded in the studied fluids with additional third surface, it is concluded that an increase in the vapor pressure (activity) will indicate promotion of gas hydrate formation while a decrease in the vapor pressure (activity) will indicate inhibition of gas hydrate formation.

Consequently, it appears that the measurement of the vapor pressure is an adequate tool to evaluate the potential for hydrate formation of a given aqueous system. In fact, the magnitude of enhancement changes are amplified in the surface tension measurements suggesting that surface tension might be a better indicator of hydrate promotion. However, the application of both methods have a common limitation. Both the vapor pressure and the surface tension would not be useful to predict inhibition in the presence of alcohols. Alcohols are known to increase both the vapor pressure and surface tension of the aqueous solutions but inhibit the formation of hydrates.

Another important result of this study, is that the inhibition of gas hydrate formation is an ordering (entropy) effect while promotion is an energetic (enthalpy) effect.

RECOMMENDATIONS FOR FUTURE WORK

The unusual elevation of the vapor pressure generated skepticism and concerns (24). There is concern that an elevation of the vapor pressure violates the laws of thermodynamics. The rationale behind this concern is that an elevation of the vapor pressure corresponds to a maximization of the free-energy rather than a minimization. Another concern is that a vapor pressure greater than that of water means an activity of the aqueous solution greater than one, and people feel that this is not possible. Finally, there is concern that the vapor pressure increase could be attributed to experimental errors and deficiencies in the experimental procedure. The argument is that, the vacuum pulled prior to any measurement is insufficient and that there is outgassing during the measurement generating the observed increase.

Numerous experiments have shown that the vapor pressure of a solvent at a given temperature is lowered by the presence of a non-volatile solute. The theoretical analysis of this phenomenon is expressed through the Gibbs-Duhem equation which assumes a homogeneous solution phase. In our case, the heterogeneity of the system is obvious. The water in presence of bentonite forms a gel while in the drilling fluid some of the water is adsorbed onto the clays, some water solvated by the polymer, and some water remains free. Therefore, fluids with additional third surface are not homogeneous solutions and consequently, the Gibbs-Duhem equation should not apply. Also, the vacuum pump used, is capable of pulling a vacuum of 0.0001 Torr suggesting that an acceptable vacuum was reached during this experimental effort. Finally, the surface tension measurements backed the vapor pressure results.

However, to settle the arguments presented against the possibility of an increase of the vapor pressure of a solvent, there is a need to extend the experimental efforts as follows:

-Improve the experimental procedure by insuring the proper evacuation of the flasks and lines in the system.

-Confirm the experimental data in an improved system, and extend the investigation to PHPA, known as a gas hydrate formation promoter. Also, evaluate the surface tension of this aqueous system and compare with results presented here.

REFERENCES

1) Hammerschmidt, E.G. Ind. Eng. Chem. 1934, 26, 851.

2) Makogon, Y. F. Hydrates of Natural Gas;Penwell: Tulsa, OK, 1981

3) Claussen, W. F. J. Phys. Chem. 1951, 19, 259.

4) Claussen, W. F. J. Phys. Chem. 1951, 19, 1425

5) Von Stackelberg, M.; Muller, H. R. J. Phys. Chem. 1951, 19, 1319

6) Jones, R. D.; Sherman, J., Offshore. 1986, 6, 27.

7) Wooley, G. R.; Giuissani, A. P.; Van Schaayk, F. 5th Annual Offshore Mechanics and Arctic Conference, Japan, 1986.

8) Barker, J. W.; Gomez, R. K. SPE/IADC Drilling Conference, New Orleans, 1987.

9) Ouar, H.; Wildeman, T. R.; Sloan, E. D. Final Report submitted to CONOCO, 1986.

10) Ouar, H.; Cha, S. B.; Inserni, T.; Wildeman, T. R.; Sloan, E. D. Final Report submitted to DEA 30, 1988.

11) Cha, S. B. M. S. Thesis, Colorado School of Mines, 1988.

12) Cha, S. B.; Ouar, H.; Wildeman, T. R.; Sloan, E. D. J. Phys. Chem. 1988, 92(23), 6492

13) Lai, D.; Dzialowski, A. K. SPE/IADC Drilling Conference, New Orleans, 1989.

14) Hale, A. H.; Dewan, A. K. R. SPE/IADC Drilling Conference, New Orleans, 1989.

15) Lewis, G. N.; Randall, M. Thermodynamics; McGraw-Hill, 1961.

16) Nielsen, R. B.; Bucklin, R. W. Hydrocarbon Processing. April 1983; p.71.

17) Erickson, D. D., M. S. Thesis, Colorado School of Mines, 1983

18) Nguyen, T. H., M. S. Thesis, Colorado School of Mines, 1986

19) Deaton, W. M.; Frost Jr., E. M. Monograph 8. Bureau of Mines, 1946.

20) de Roo, J. L.; Peters, C. J.; Lichtenthaler, R.N.; Diepen,G.A. AIChE J. 1983, 29(4), 651.

21) Skoog, D. A.; West, D. M.; Holler, F. J. Fundamentals of Analytical Chemistry; Saunders College Publishing,

22) Kaufmann, D. W. Sodium Chloride; Reinhold, New York, 1960.

23) International Critical Tables

24) Sloan, E. D. Personal Communication.

25) Davidson, D. W. in Water:A Comprehensive Treatise. F.Franks, Plenum Press, New York, 1973

26) Holder, G. D.; Zetts, S. P.; Pradhan, N. Reviews in Chemical Engineering. 1988, 5.

Appendix A

Theory of Gas Hydrates

Natural gas hydrates are inclusion compounds or clathrates. Inclusion compounds are physical combinations in which one component fits into a cavity formed by the other. A combination of considerable strength can occur when the shape and form of the guest molecule closely matches the cavity formed by the host molecules. No ordinary chemical bonding between the atoms of the guest and the host are needed for stabilization. In fact, the clathrate is stabilized by van der Waals forces of interaction between the guest molecule and the cavity formed by a lattice of host molecules. In the case of gas hydrates, the gas molecules are the guest species and the water molecules form the host lattice. Gas hydrates are non-stoichiometric solid solutions. The clathrate structure grows under metastable conditions, with the inclusion of natural gas molecules into the cavities occuring at the same time that the cavities are formed from water molecules. The translational degree of freedom of the guest gas molecule is dictated by the cavity size relative to the molecule. The degree of translation and rotation of the guest molecule ranges from that of a gas to that of a dense fluid (25) depending upon the molecular size.

Claussen (3, 4) suggested structures of gas hydrates that were verified through X-ray diffraction by Von

Stackelberg and Muller (5). Von Stackelberg and Muller have shown through X-ray diffraction that thw water molecules in these clathrates are linked together through hydrogen bonding. A ring structure of five water molecules is formed rathe than the six molecule ring typical of ice. These five member rings are faces which join together to form dodecahedra. Since no arrangement of dodecahedra can completely fill a space (25), some interstitial spaces remain. It is in these interstitial spaces existing in the dodecahedra, that the guest molecules are found.

These X-ray crystallographic studies have also shown that gas hydrates crystallize in one of two structures, Structure I or Structure II, depending upon the shape and the size of the guest molecule. The basis for each structure is a pentagonal dodecahedron shown in Figure 4. Each circle represents an oxygen atom and the lines represent molecular bonds and hydrogen bonds which hold the water molecules together. A fourth line not shown extends for each oxygen atom to join to adjacent cavities. For each oxygen atom, two lines represent molecular bonds and two lines represent hydrogen bonds. In the Structure I hydrate, pentagonal dodecahedra are arranged together with tetrahedra to form twelve pentagonal and two hexagonal faces, enclosing two small and six large cavities of 3.94 A and 4.30 A

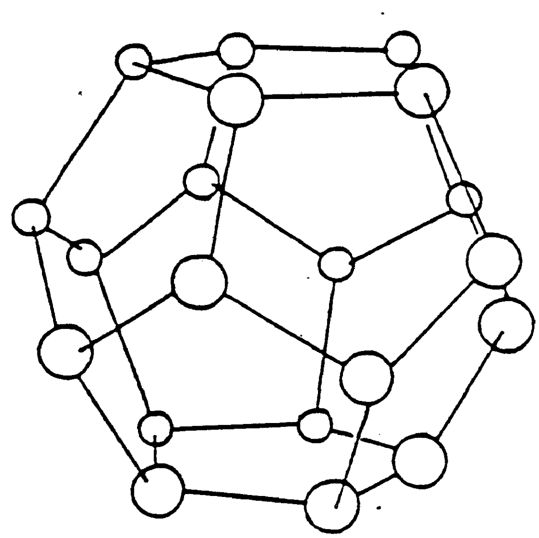

Figure 4. A Pentagonal Dodecahedron-One of Four Cavities of Natural Gas Hydrates. (Redrawn from Makogon)

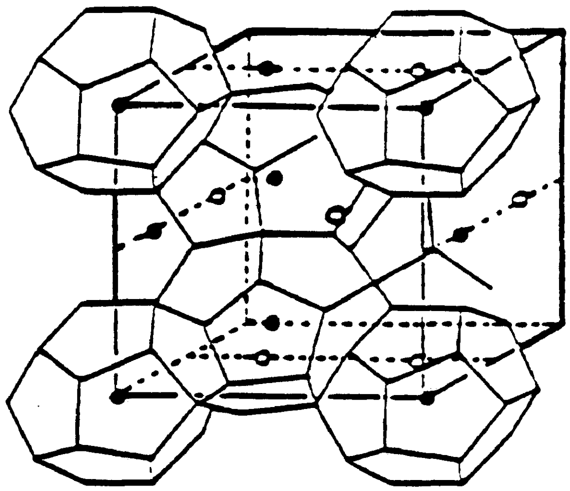

Figure 5. Unit Cell Configuration of Structure I Gas Hydrate. The Large Dots Represent Guest Gas Molecules. (Redrawn from Makogon)

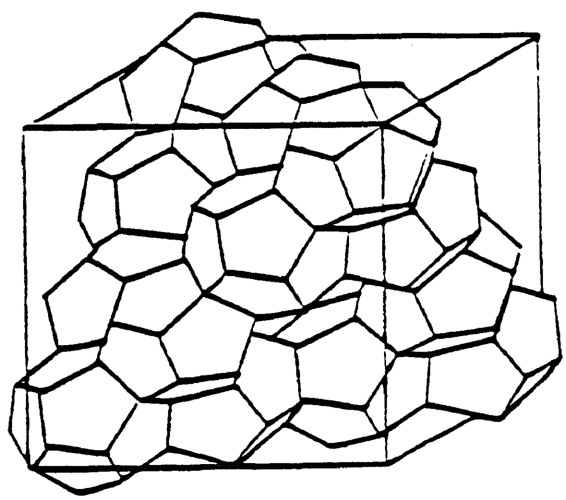

Figure 6. Unit Cell Configuration of Structure II Gas Hydrate. (Redrawn from Makogon)

diameter respectively. Forty six molecules of water are needed for the construction of this lattice.

When all eight cavities are occupied a ratio of 5.75 water molecules per gas molecule is obtained. The resulting body centered cubic is shown in Figure 5.

In the Structure II hydrate, pentagonal dodecahedra are packed together with hexahedra to form twelve pentagonal and four hexagonal faces, enclosing sixteen small and eight large cavities of 3.91 A and 4.73 A diameter respectively. One hundred thirty six molecules of water form this lattice. When all cavities are filled a ratio of 5.67 water molecules per gas molecule is obtained. The resulting diamond lattice cell structure is shown in Figure 6. The properties of the gas hydrate lattices are described in Table 7.

Natural gas molecules required to stabilize the hydrate lattice must be smaller than pentane in order to fit into the cavities of either Structure I or Structure II. The Structure I is primarily composed of methane oe ethane hydrocarbon gases, CO_2, H_2S, while the Structure II is stabilized by propane and isobutane, yet contain the smaller components.

Structure II is more stable than Structure I due to the approximately tetrahedral angles found in Structure II hydrate. This stability of Structure II hydrates allow them to exist in a wider range of natural environments. Holder (26) provides an excellent review of the physical and chemical nature of gas hydrates.

TABLE 7

Hydrate Lattice Properties.

	Structure I	Structure II
Unit cell size (Angstrom)	12.03	17.31
Number of Dodecahedra	2	16
Number of Tetrakaidecahedra	6	0
Number of Hexakaidecahedra	0	8
Water molecule/Unit cell	46	136
Cavities (cages)/Unit cell		
Small	2	16
Large	6	8
Cavity Radius (Angstrom)		
Small	3.94	3.91
Large	4.30	4.73
Typical gases which form in each cavity of this structure.		
S = Small	methane(S)	argon (S)
L = Large	ethane (L)	propane (L)

Appendix B

Sodium Chloride Vapor Pressure Data

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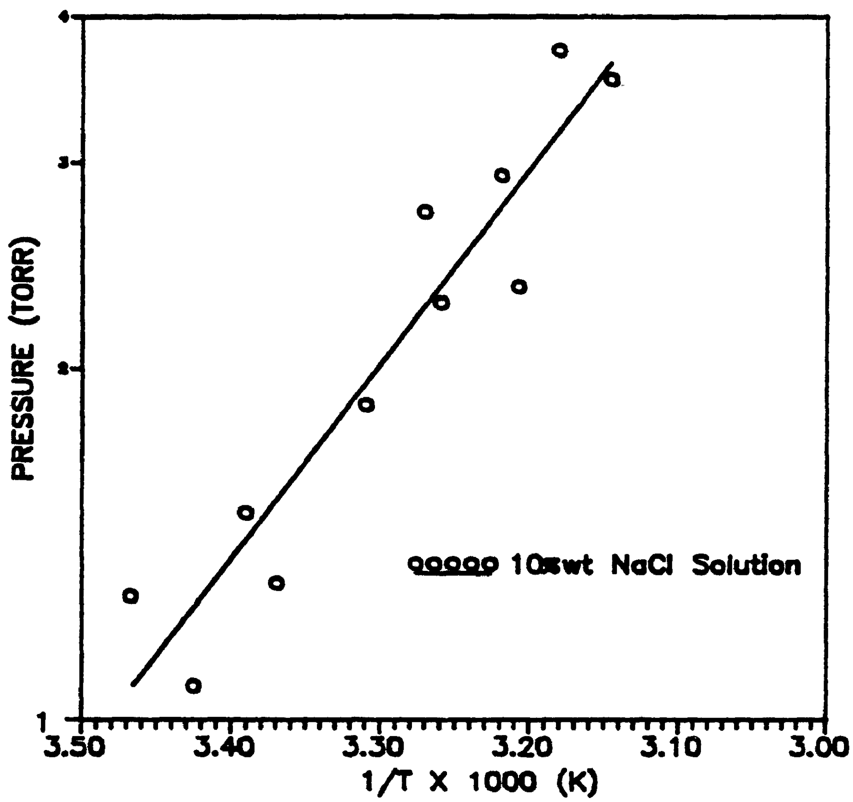
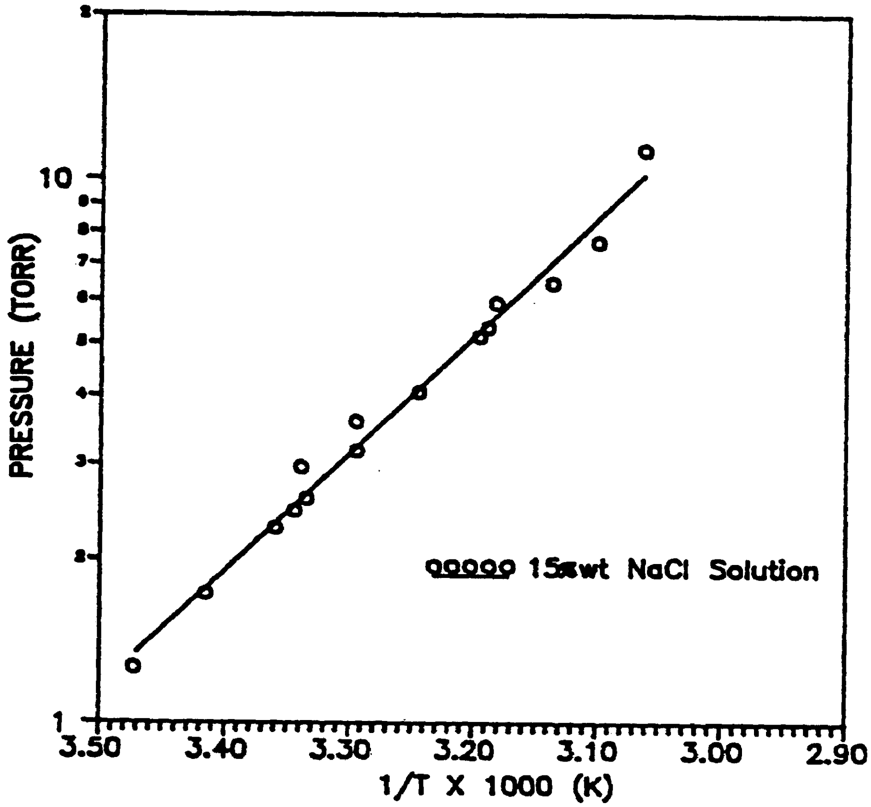
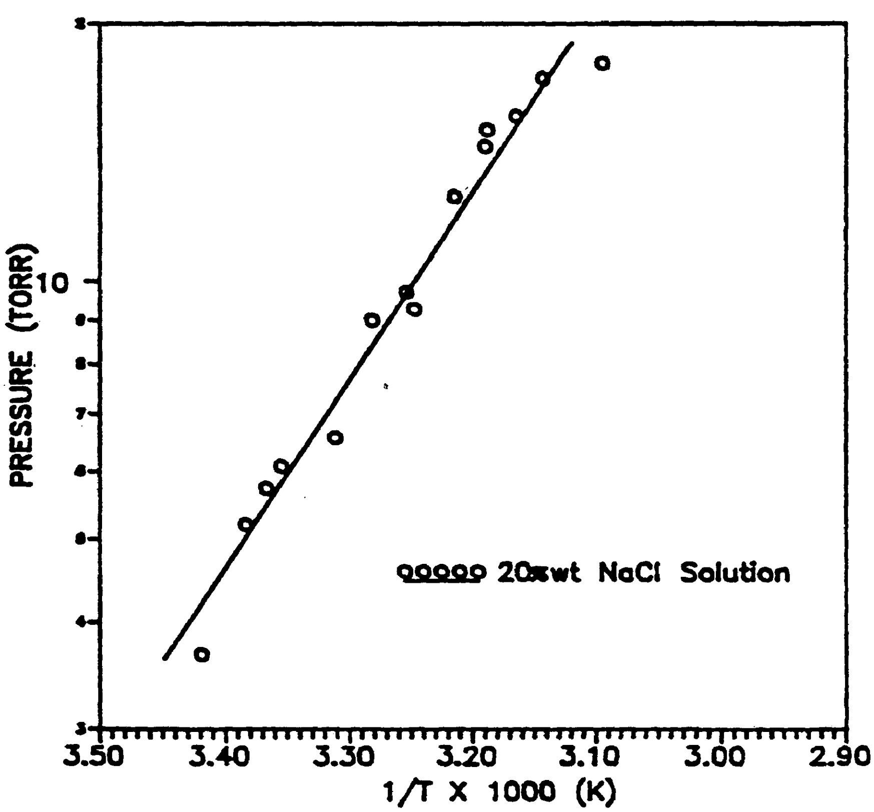
Appendix B1

Vapor Pressure Measurement of

NaCl solutions against Vacuum




PRESSURE (TORR)
10
1
3.50
3.40
3.30
3.20
3.10
3.00
2.90
1/T X 1000 (K)
ooooo 15%wt NaCl Solution

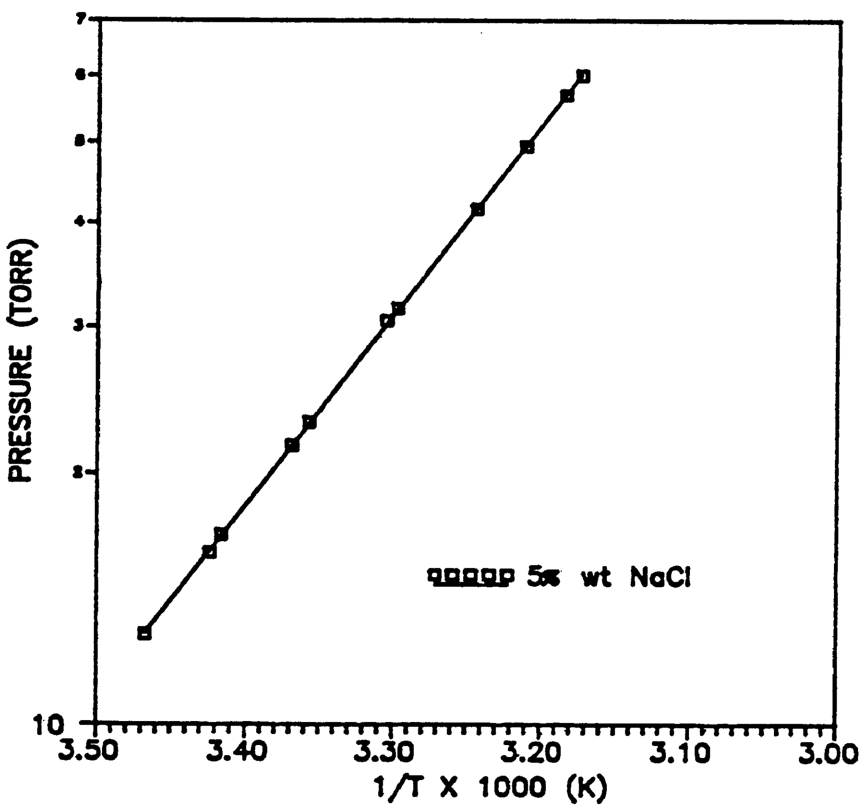

PRESSURE (TORR)
10
3.50
3.40
3.30
3.20
3.10
3.00
2.90
1/T X 1000 (K)
ooooo 20%wt NaCl Solution

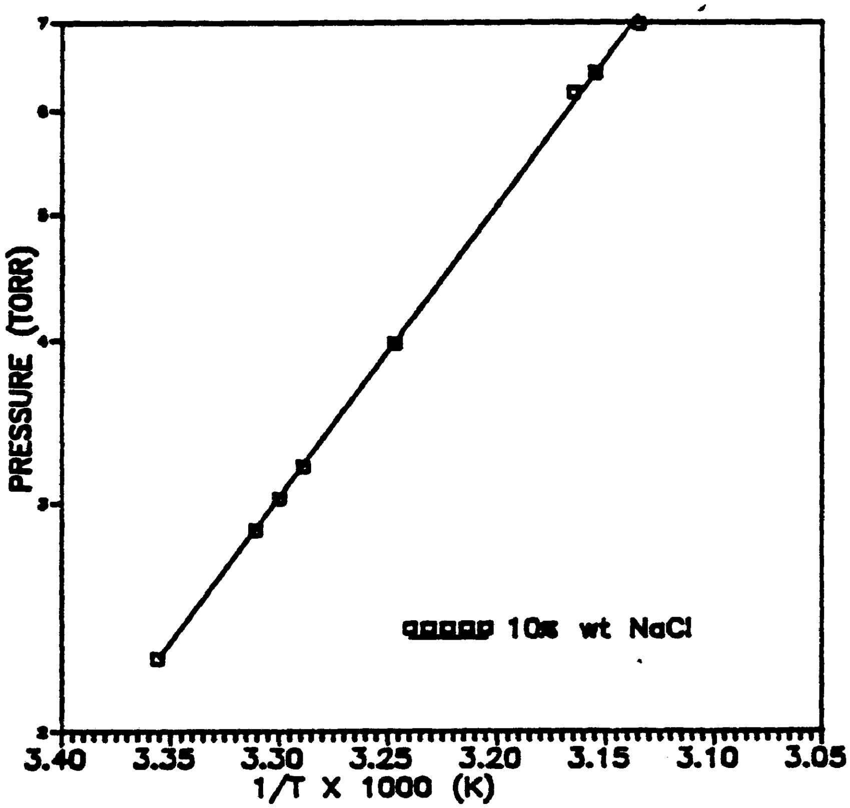
Appendix B2

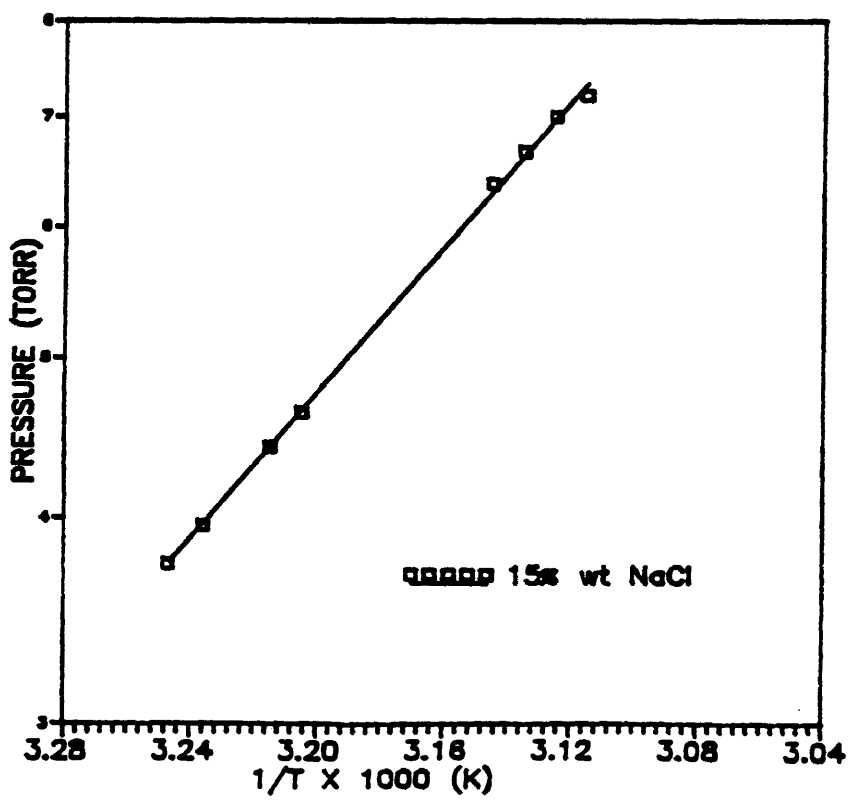
Vapor Pressure Measurement of

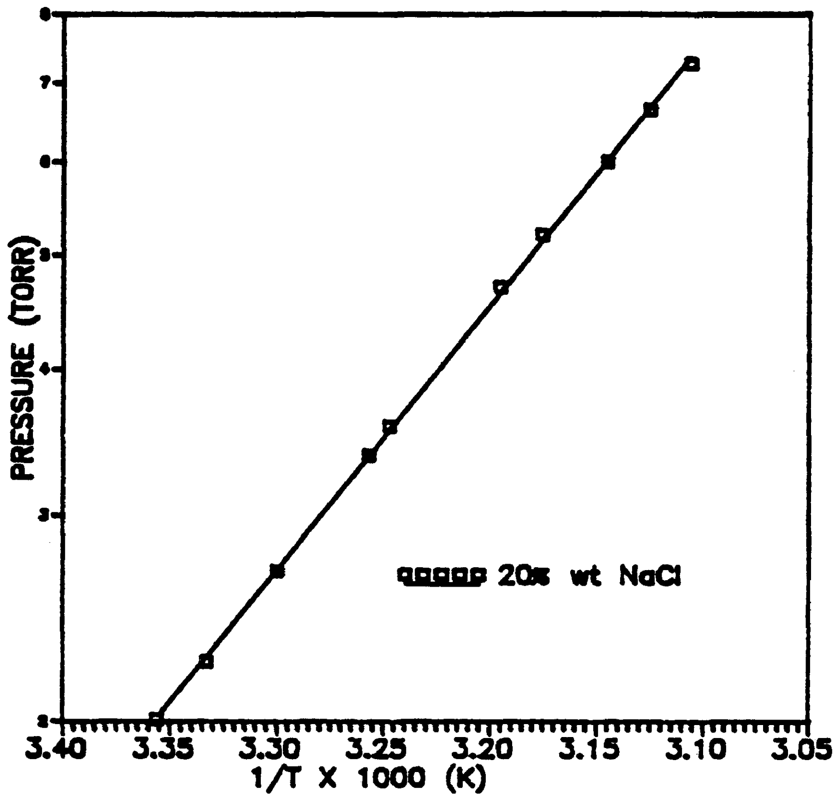
NaCl solutions relative to water

The vapor pressure represented in the following plots is evaluated from the relative measurement to water. The vapor pressure of the salt solution is determined as the difference between the water vapor pressure minus the relative difference measured experimentally.




PRESSURE (TORR)
10% wt NaCl
3.40 3.35 3.30 3.25 3.20 3.15 3.10 3.05
1/T X 1000 (K)


PRESSURE (TORR)
15% wt NaCl
3.28 3.24 3.20 3.16 3.12 3.08 3.04
1/T X 1000 (K)


PRESSURE (TORR)
1/T X 1000 (K)
3.40
3.35
3.30
3.25
3.20
3.15
3.10
3.05
20% wt NaCl

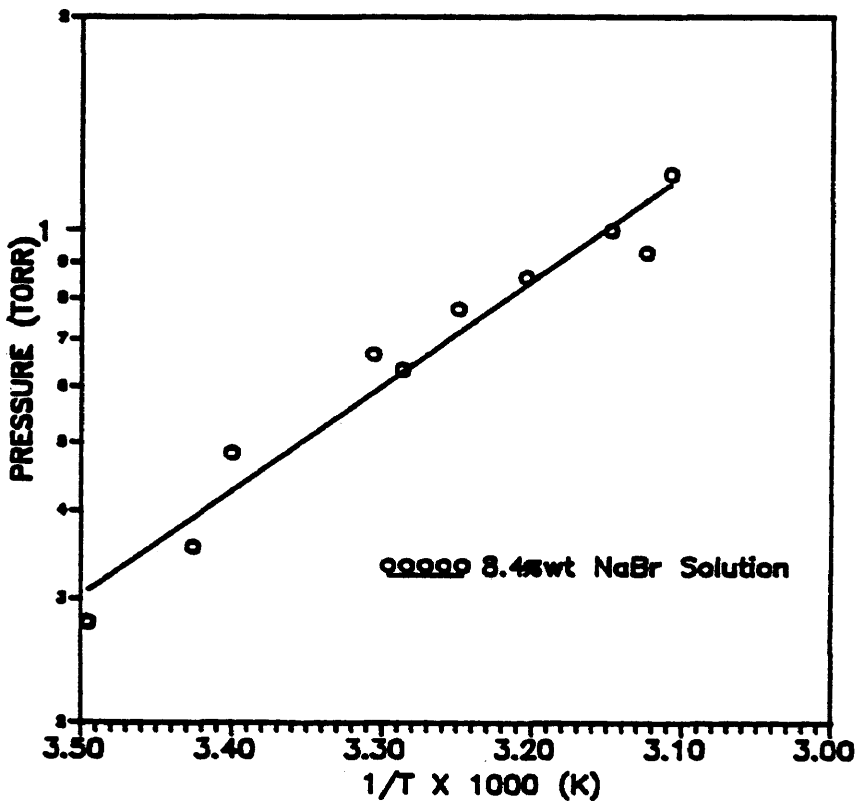
Appendix C

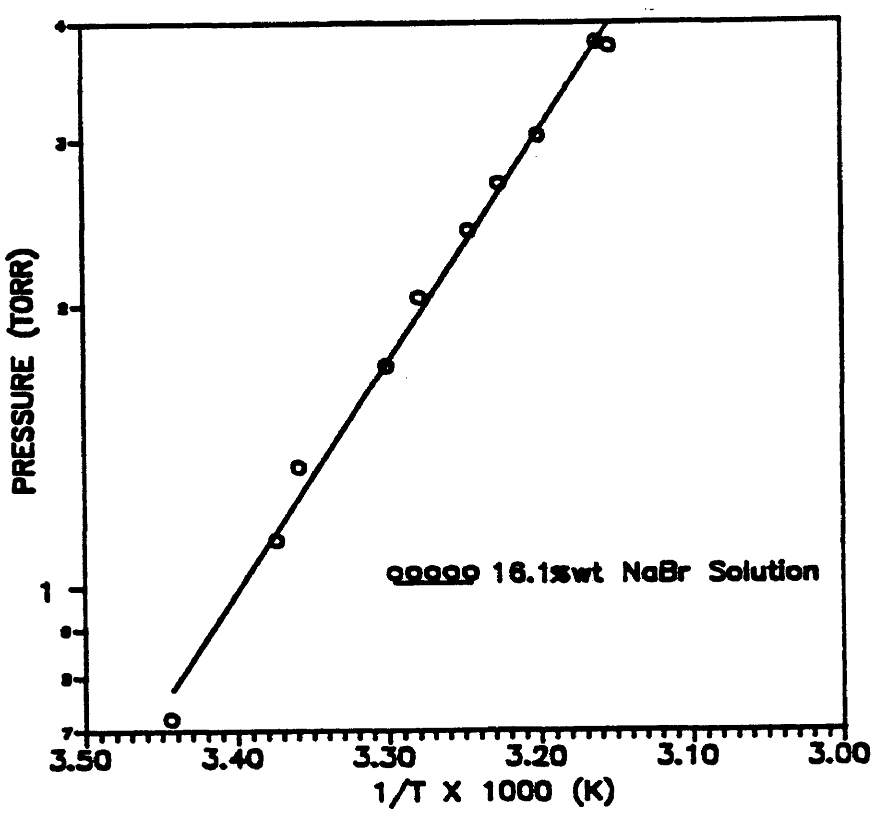
Sodium Bromide Solutions Vapor Pressure Data

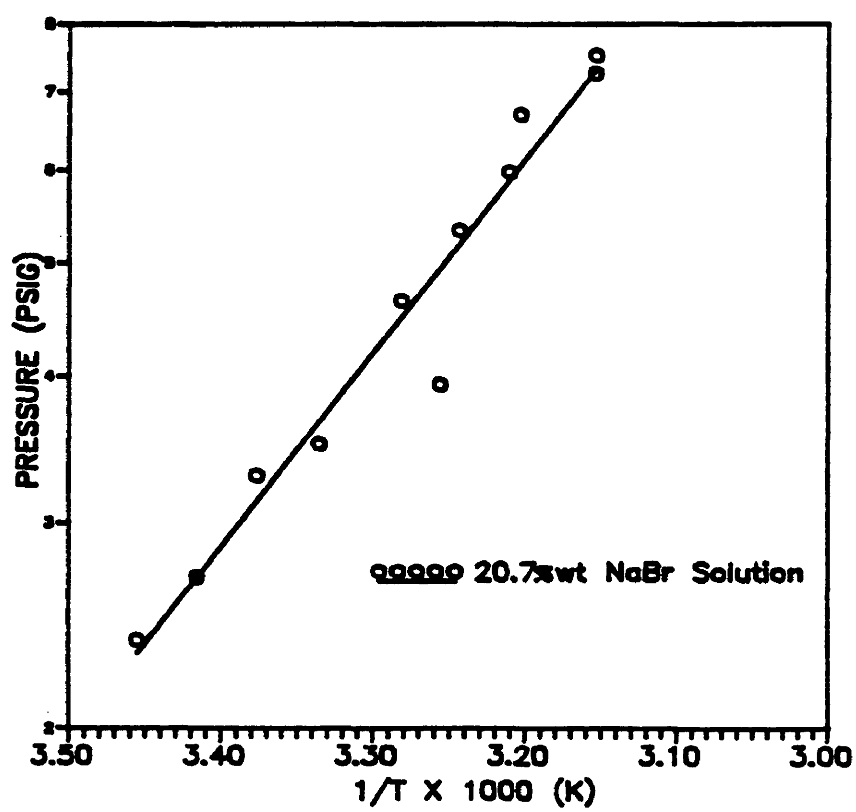
Appendix C1

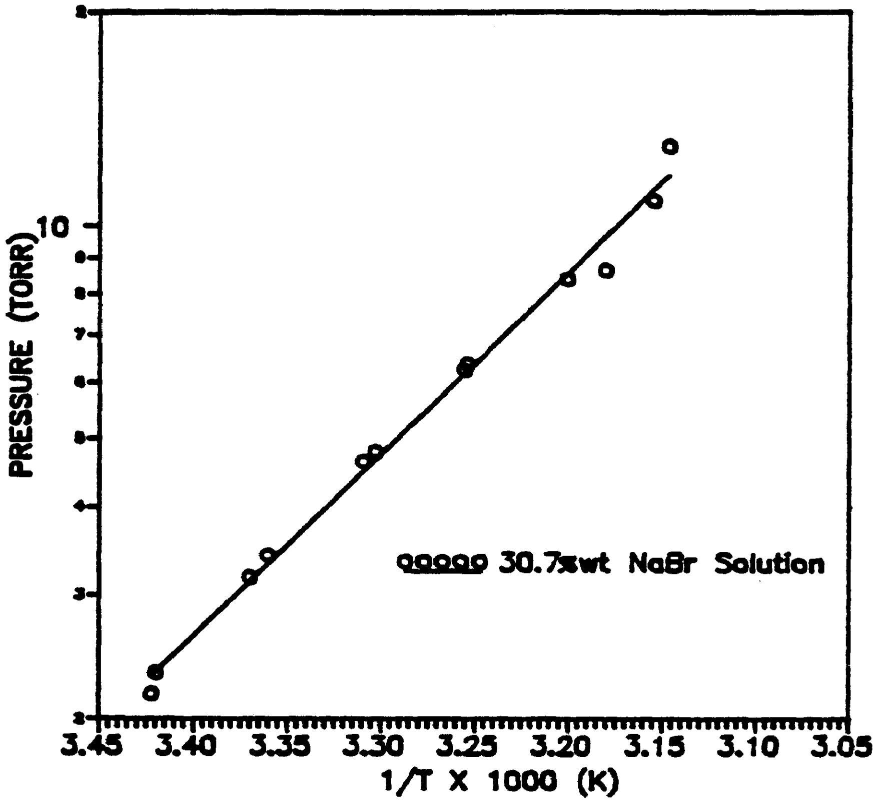
Vapor Pressure Measurement of

NaBr solutions against Vacuum




PRESSURE (TORR)
1
ooooo 16.1%wt NaBr Solution
3.50
3.40
3.30
3.20
3.10
3.00
1/T X 1000 (K)

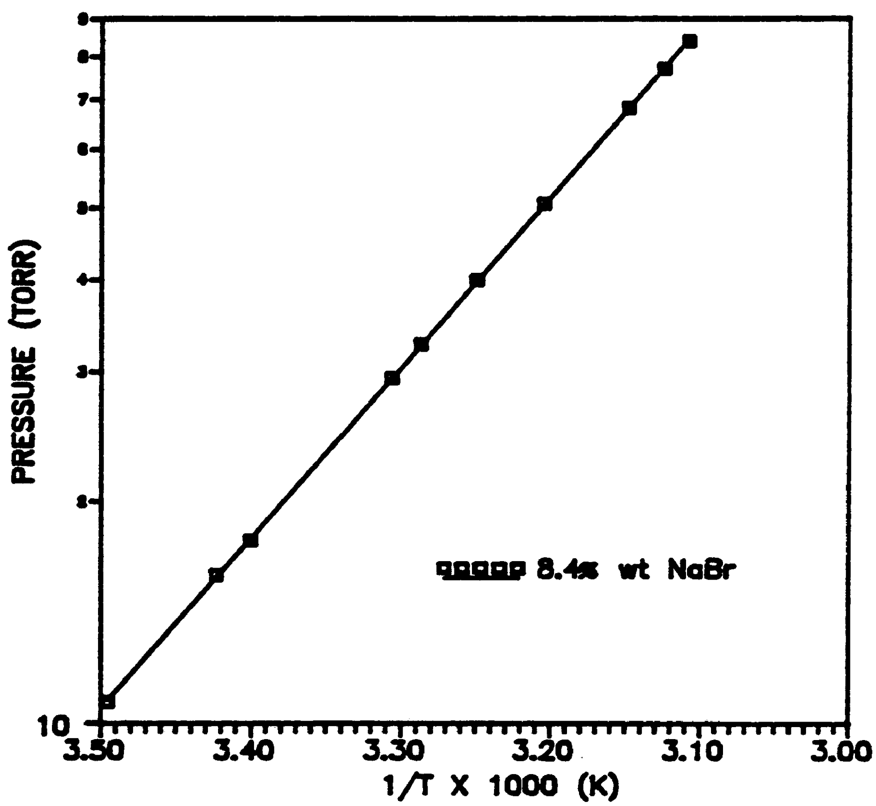

PRESSURE (PSIG)
ooooo 20.7%wt NaBr Solution
3.50
3.40
3.30
3.20
3.10
3.00
1/T X 1000 (K)

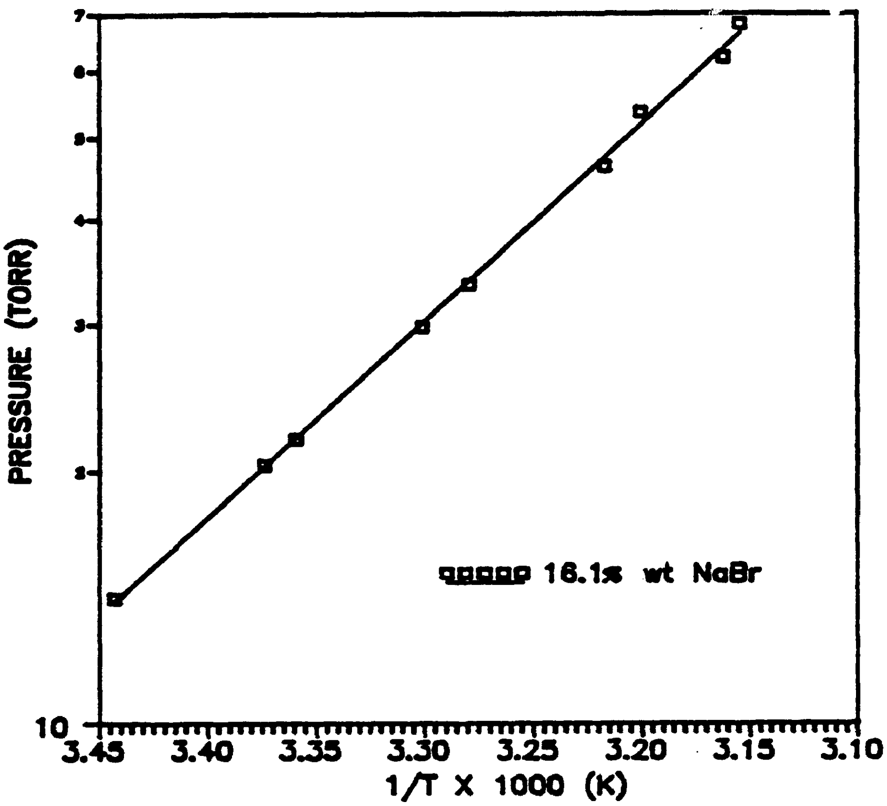

PRESSURE (TORR)
10
9
8
7
6
5
4
3
2
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.10
3.05
1/T X 1000 (K)
30.7%wt NaBr Solution

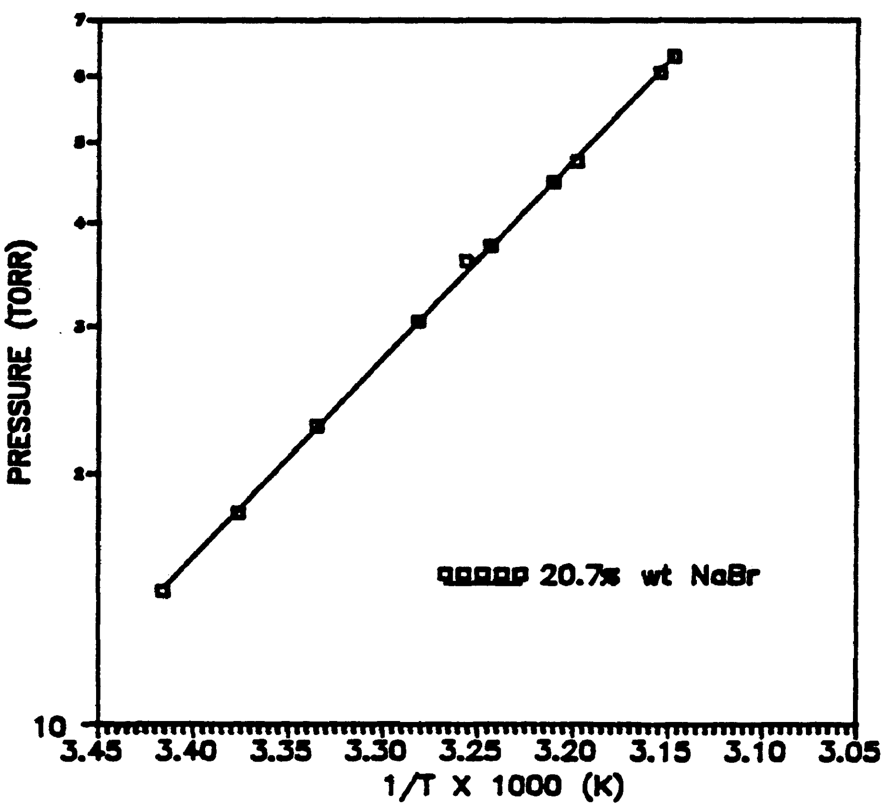
Appendix C2

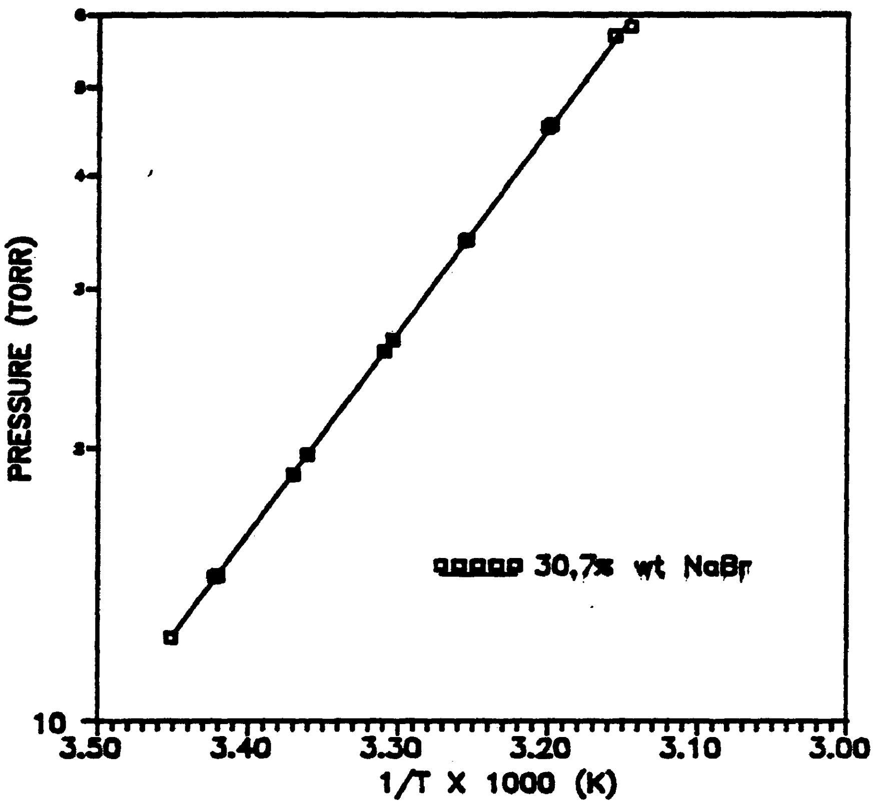
Vapor Pressure Measurement of

NaBr Solutions relative to Water




PRESSURE (TORR)
10
3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10
1/T X 1000 (K)
16.1% wt NaBr


PRESSURE (TORR)
10
3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10 3.05
1/T X 1000 (K)
20.7% wt NaBr


PRESSURE (TORR)
10
3.50
3.40
3.30
3.20
3.10
3.00
1/T X 1000 (K)
30,7% wt NaBr

Appendix D

Vapor Pressure Measurement of Drilling Fluids against vacuum at room temperature

	P (Torr)	T (C)
A2 20%NaCl	16.500	22.5
A2 12%NaCl	18.704	22.5
MUD 13	21.474	23.4
AH2 20%NaCl	17.432	22.9
AH1 20%NaCl	16.246	21.6
A3 20%NaCl	18.452	24.6
A1 20%NaCl	17.292	23.4
A2 30%NaBr	20.354	26.8
A2 20%NaBr	17.864	24.6

Composition of Drilling Fluids

Component	A2	A1	A3	AH1	AH2	MUD13
Water	349.0	349.0	349.0	349.0	349.0	335.6
NaCl	82.0	82.0	82.0	82.0	82.0	
Sea salt	6.0	6.0	6.0	6.0	6.0	
Bentonite	13.75	13.75	13.75	------	------	14.5
PHPA	0.63	0.63	-----	0.63	0.63	1.0
DSL	0.63	0.63	0.63	0.63	0.63	
XCD	0.63	-----	0.63	0.63	0.63	
Rev Dust	25.0	25.0	25.0	25.0	25.0	20.0
Barite	205.4	205.4	205.4	------	205.4	

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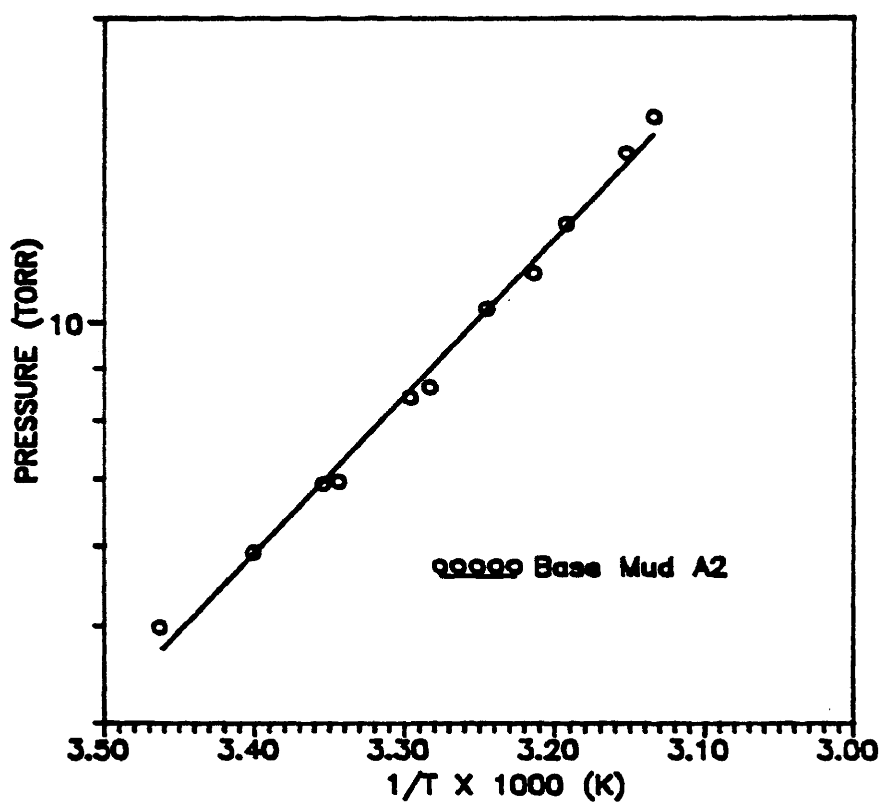
Appendix E

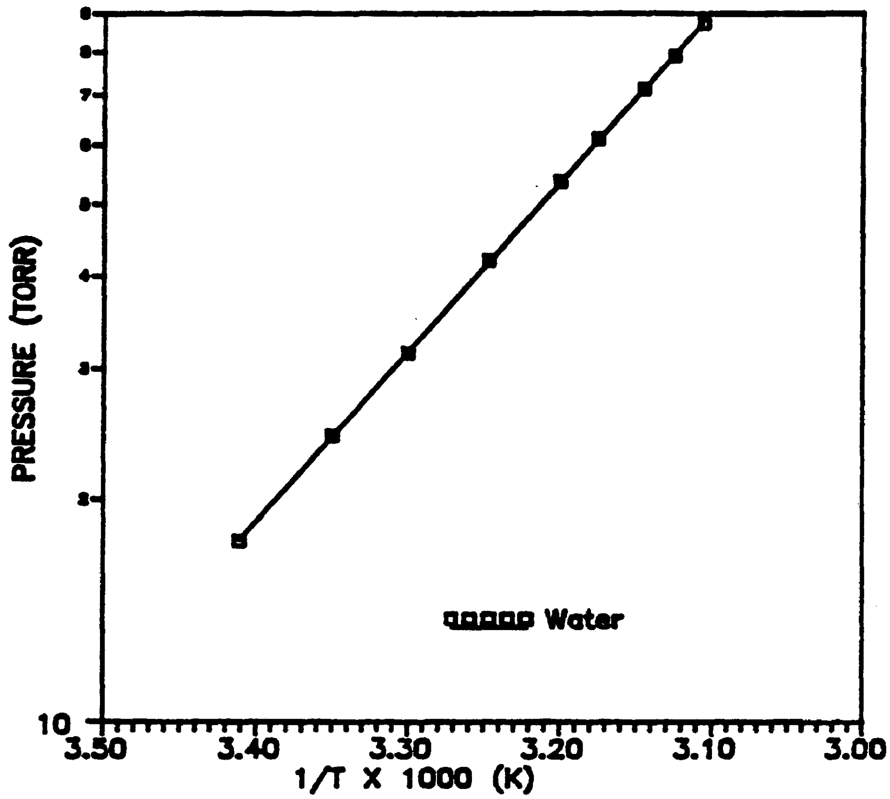
Vapor Pressure Measurement of

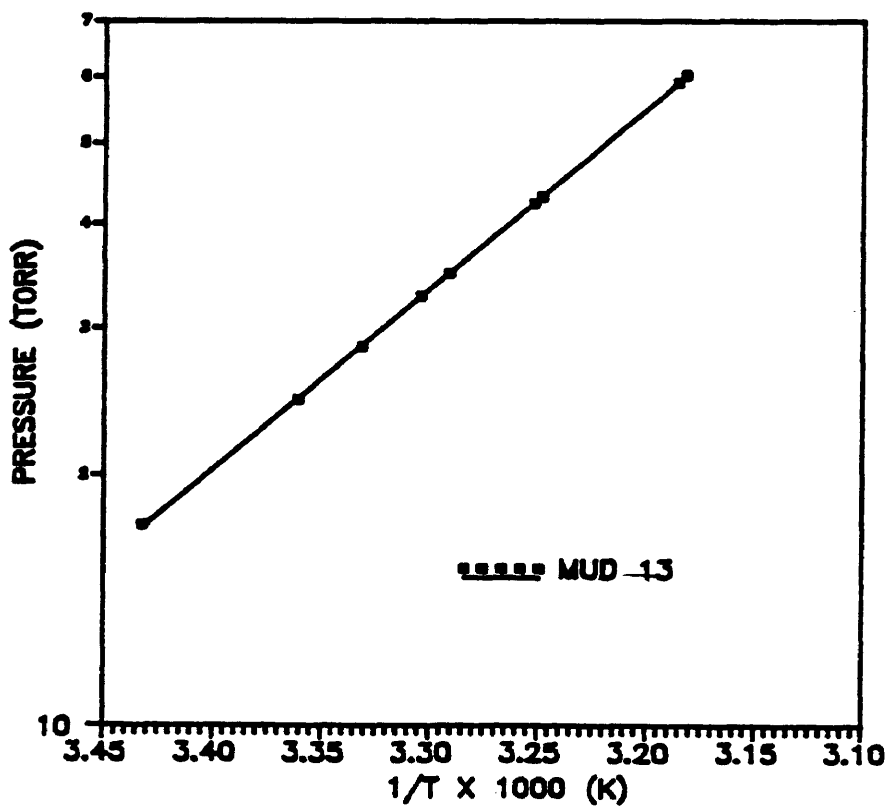
Base Mud A2 against Vacuum

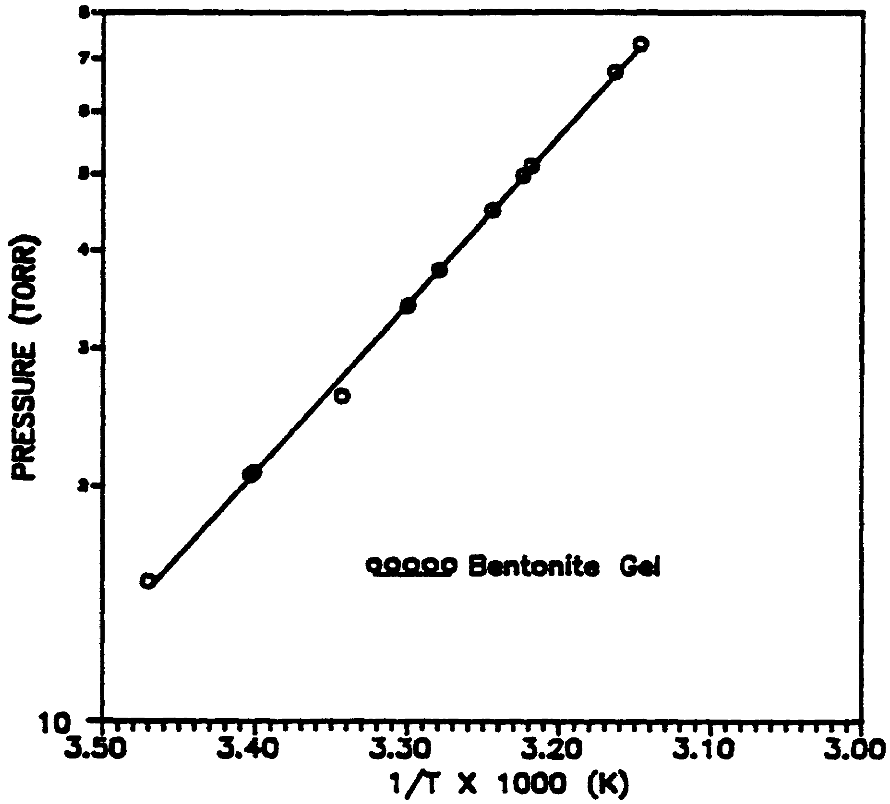


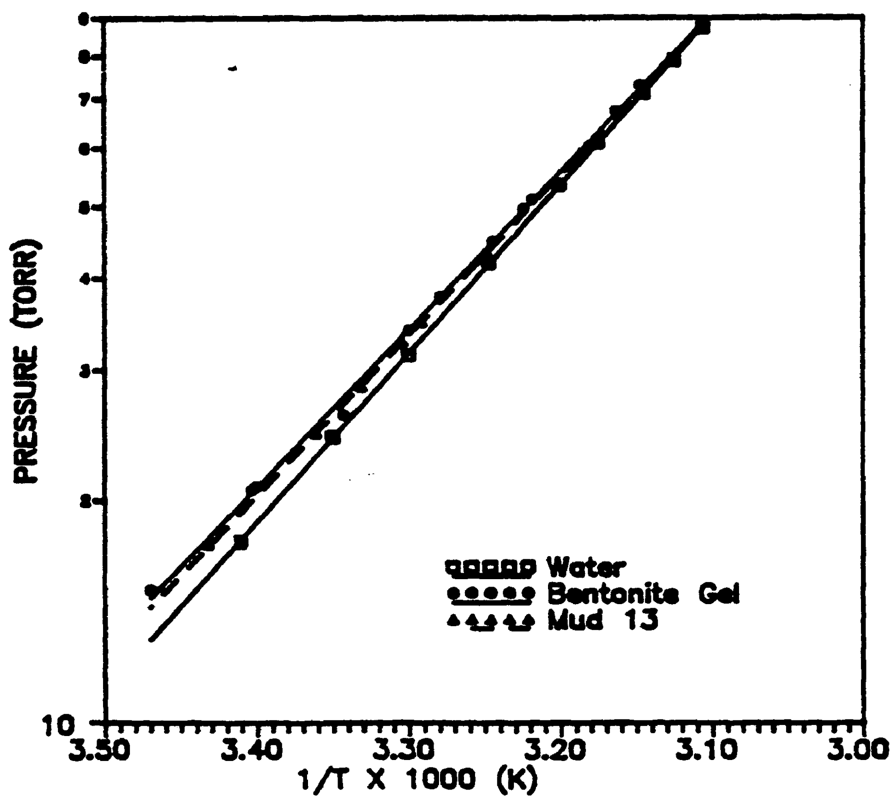
Appendix F

Vapor Pressure Measurement of Drilling Fluids relative to water


PRESSURE (TORR)
Water
10
3.50
3.40
3.30
3.20
3.10
3.00
1/T X 1000 (K)


PRESSURE (TORR)
MUD-13
10
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.10
1/T X 1000 (K)


PRESSURE (TORR)
1/T X 1000 (K)
3.50
3.40
3.30
3.20
3.10
3.00
10
Bentonite Gel


PRESSURE (TORR)
1/T X 1000 (K)
3.50
3.40
3.30
3.20
3.10
3.00
10
Water
Bentonite Gel
Mud 13

Appendix G

Relation between Vapor Pressure and Activity

Assuming no solute vaporization:

$$Y \quad P = \quad Xi \ Pi \quad \exp \quad VdP/RT$$

where:

$Yi = 1.0$ (pure component water)

$i = 1.0$ low pressure P

$i = 1.0$ low pressure Pi

$\exp VdP/RT = 1.0$ low P

Therefore:

$$P = Xi \quad Pi$$

$$P = ai \ Pi$$

$$ai = P/Pi$$

In the presence of a non-volatile solute, the activity of a solvent is equal to the ratio of the vapor pressure of the solution over the initial vapor pressure of the solvent.

Appendix G1

Activity Calculation

Using vapor pressure data for NaCl solutions and pure water a second order polynomial fit of the activity as function of absolute temperature and weight % NaCl was developed.

ai=1.00055 -.21236*10^-4*T -.597389*10^*X +.757617*10^-7*T^2 +.894371*10^-5*T*X -.22013984*10^-3*X^2

Appendix G2

Hydrate Formation Prediction

Hydrate formation requires the presence of: 1) water, 2) gas, 3)low temperature, and 4) high pressure.

During drilling operations or natural gas processing, the composition of the gas, the temperature and pressure are determined by the operational conditions and therefore not much can be done to alterate these hydrate formation parameters. Therefore, the only parameter which can affect the hydrate formation conditions is the water phase. The activity of the water represents a measure of the capability of water to form or not form hydrates. Consequently, the knowledge of the activity of the water will allow us to evaluate the potential for hydrate formation. Predictive models for hydrate formation have been developed based on statistical thermodynamics, including activity as a parameter. A computer model developed in our laboratory and marketed under CSMHYD, is one of the more widely used.

The following sequential work is needed to predict hydrate formation from colligative properties:

- Measure vapor pressure of aqueous system
- Calculate activity from vapor pressure data
- Use CSMHYD to predict the hydrate formation

condition of pressure and temperature for a given gas composition.

- Compare the predicted data with the experimental data produced in the high pressure hydrate formation system.

Appendix H

Experimental Procedure

1) Prepare solutions to be analyzed
2) Pull vacuum on flask alone for 5 minutes
3) Pull vacuum on flask and line to barocel for 5 minutes
4) Close valve to flask, keep pulling vacuum on line to barocel for 2 hours while Establishing zero on readout.
5) Open flask to barocel. Measure vapor pressure of solution against vacuum as function of temperature. The variation of temperature should be stepwise. It is recommended to take a measurement every 5 C, in a range from 20 to 50 C. At each step, the temperature should be maintained constant for at least 30 minutes to allow for equilibrium. The vapor pressure is measured as the temperature is increased, and then decreased over the range of interest. The vapor pressure value taken after 30 minutes, is the value reported.
6) In the case of measurement relative to water, both flasks are connected to the barocel and the steps 1 to 5, are carried out on both sides of barocel and flasks simultaneously. Prior to the relative measurement, as a check, the vapor pressure of the water and the solution tested are both individually measured against vacuum by step 5.