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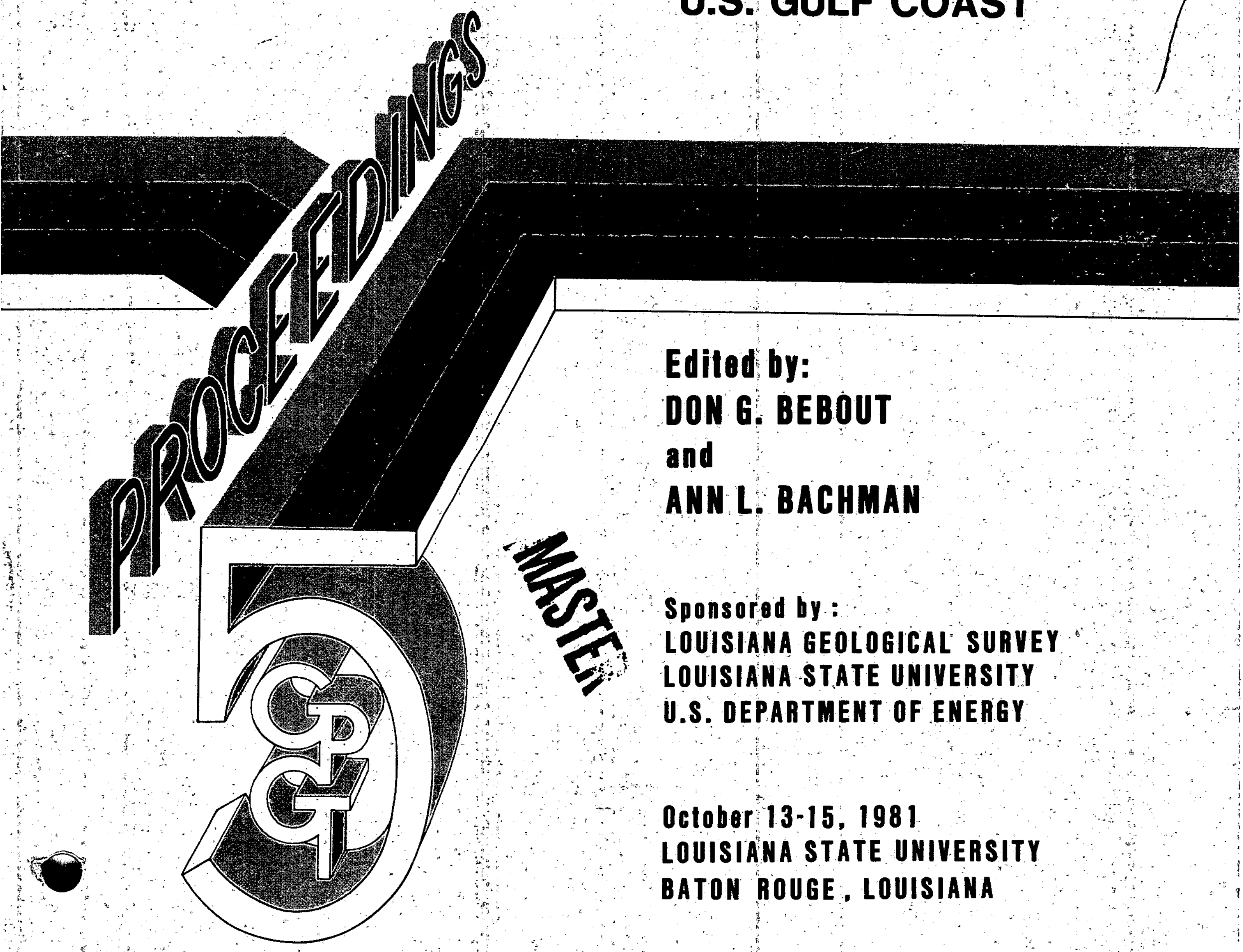

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Edited by:
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Sponsored by:
LOUISIANA GEOLOGICAL SURVEY
LOUISIANA STATE UNIVERSITY
U.S. DEPARTMENT OF ENERGY

October 13-15, 1981
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA

Contract No. DE-FG08-81NV10186

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A CORRELATION OF PUBLISHED DATA ON THE SOLUBILITY OF METHANE IN H_2O-NaCl SOULTIONS

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ABSTRACT

A new correlation of the available published data for the solubility of methane in water was developed, based on fundamental thermodynamic relationships. An empirical relationship for the salting-out coefficient of NaCl for methane solubility in water was determined as a function of temperature. Root mean square and average deviations for the new correlation, the Haas correlation, and the revised Blount equation are compared.

INTRODUCTION

This paper presents the results of work done at LSU with the primary objective of providing the LSU techno-economic computer model of a GP/GT resource with a subroutine, SOLUTE, to calculate the methane content of a geopressured brine at a given temperature, pressure, and salinity.

Early Correlations

At the time the LSU project was initiated in June, 1979, the curves of Culberson-McKetta (1951) were in general use for predicting the solubility of methane in water, and the effect of salt content on methane solubility was estimated by curves of Isokrari (1976), which used a correction factor proposed by Brill and Beggs (1975). An empirical polynomial fit of the Culberson-McKetta data was proposed by Garg, et al (1977), and an analytical expression for the salt correction factor was given by Prichett, et al (1979) which, based on data for salt solutions from O'Sullivan and Smith (1970), was invariant with temperature and pressure.

Correlation of Haas

A semi-empirical correlation for methane solubility in water was proposed by Haas (1979), based on the data of Culberson-McKetta (1951), Sultanov, et al (1972), and Duffy, et al (1961). The Haas correlation procedure involved subtracting the vapor pressure of pure water from the total pressure to estimate the partial pressure of the methane, $P(CH_4)$, and then plotting the methane content of the water, $x(CH_4)$, vs. Ln $[x(CH_4)/p(CH_4)]$ to obtain straight lines at constant temperature. The slopes and intercepts of these lines were fit to polynomials in t, °C. Haas proposed that, for water-NaCl solutions, a constant salting-out coefficient of 0.11 based on the data of O'Sullivan and Smith (1970) be used until additional data became available.

To implement his correlation, Haas wrote a FORTRAN program, XCH4, which calculates the methane solubility in ppm by an iteration procedure given temperature (°F), pressure (psia), and salinity (ppm NaCl) as inputs.

Published Data on Methane Solubility

Namiot, et al (1979), Price (1979), and Blount, et al (1979) published data after the Haas correlation was developed. A summary of published data is shown in Table 1.

Correlation of Blount

Blount, et al (1979) developed by linear regression an empirical equation to fit his solubility data. Unfortunately, methane solubilities predicted by this equation were up to 25% higher

Table 1. Published Data on Methane Solubility in Water and Water-NaCl Solutions

Authors	Number of Data Points	Temperature, ° Celsius	Pressure, atmospheres	Salinity, wt %
Culberson and McKetta (1951)	72	25 - 171	20 - 690	0
Duffy, et al (1961)	--	25 and 30	3 - 50	0 - 24
O'Sullivan and Smith (1970)	50	51.1, 102.5, and 125	100 - 600	0 - 19
Sultanov, et al (1972)	71	150 - 360	50 - 1080	0
Namiot, et al (1979)	14	50 - 350	295	0 , 5.5
Price (1979)	71	154 - 354	35 - 1950	0
Blount, et al (1979) *	492	100 - 206	139 0 1534	0 - 25

* Revisions to these original data made available by Blount (1981)

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than those read from the Culberson-McKetta curves or those calculated with the correlation of Haas, indicating a basic discrepancy between the results of Blount and those of previous investigators. Recently Blount (1981) reported a revised correlation equation, which was obtained after finding and correcting a systematic error in the mathematical treatment of his raw data. The revised data of Blount were not available when the LSU correlation was performed. His revised equation predictions are, however, included in the comparisons made in Table 3. An addendum to this paper may be distributed at the conference to include the effect of the revised Blount data on the LSU correlation results.

CORRELATION OF METHANE SOLUBILITY DATA AT LSU

The status in mid-1979 for methane solubility predictions was: The Culberson-McKetta and Isokrari curves were available for hand calculations, but they were based on only a fraction of available data, and the pressure range did not extend very far into the geopressured region. The Garg and Prichett equations, although suitable for computer calculations, were only analytical expressions of the Culberson-McKetta and Isokrari curves. The Haas correlation utilized the Sultanov and Duffy data for water, and it was less empirical because of its use of methane partial pressure; but it did not improve upon the assumption of a constant salting-out coefficient, it had not included the Price, Namiot, and Blount data, and was not recommended for accurate extrapolation above 10,000 psia. Finally, the (first) Blount equation and data did not seem to agree with the previous curves and correlations.

Development of the Correlation Procedure

Mr. Leonard Coco, a graduate student in Chemical Engineering, undertook for his M. S. research project the development of a new correlation to be based on as much of the available data as possible and utilizing fundamental relationships in the equations. Since the goal of the project was a computer subprogram, extra calculations required by a fundamental approach, such as fugacities instead of partial pressures, were not considered a disadvantage, whereas a fundamentally based correlation was expected to result in a better fit of the data, more accurate extrapolation, and physically meaningful parameters. The initial version of the correlation procedure was reported at Sea Island, by Johnson (1980), with parameter values based on the data of O'Sullivan and Smith (1970), the only NaCl-water data available at that time.

The equations used by Johnson (1980) were modified and extended in the M.S. project of Coco. A brief development of the equations for correlating methane solubilities in water follows.

Equations for Vapor-Liquid Equilibria In the Methane-Water Binary System

The fundamental relationships defining vapor-liquid equilibrium conditions are:

Both phases are at temperature and pressure equilibrium:

$$T^V = T^V \qquad (1)$$

$$P^V = P^L \qquad (2)$$

Both phases are at mass transfer equilibrium:

$$f^V_{H_2O} = f^L_{H_2O} \qquad (3)$$

$$f^V_{CH_4} = f^L_{CH_4} \qquad (4)$$

The fugacities in equations (3) and (4) may be replaced by exact thermodynamic expressions to give:

$$\phi_{H_2O}\, y_{H_2O}\, P = x_{H_2O}\, \phi^s_{H_2O}\, P^s_{H_2O}\, \Phi^P_{H_2O} \qquad (5)$$

$$\phi_{CH_4}\, y_{CH_4}\, P = x_{CH_4}\, H_{CH_4} \qquad (6)$$

Only one approximation was made: In equation (5) the activity coefficient for water in the liquid phase is taken to be 1.0, since the mol fraction of water usually exceeds 0.99 for this system. In equation (6) Henry's law coefficient, H_{CH_4}, is a function of temperature, pressure, and methane content, so that no approximation is introduced through its use.

If we consider for the moment that functional relationships are available for calculating the various thermodynamic coefficients in equations (5) and (6), then they contain four unknowns: y_{H_2O}, y_{CH_4}, x_{H_2O}, and x_{CH_4}. Because the mol fractions in each phase must sum to 1.0, the unknowns can be reduced to only two (x_{CH_4} and y_{CH_4}) and the two equations can be solved by iteration to give the methane content of the liquid phase, x_{CH_4}.

Calculation of Thermodynamic Coefficients

The value of $\phi^s_{H_2O}$, the fugacity coefficient of water vapor at saturation pressure was calculated from an equation of state for pure water given by Keenan, et al (1969). Values for ϕ_{H_2O} and ϕ_{CH_4}, the fugacity coefficients for water and methane in vapor mixtures, were calculated based on an equation of state developed by Nakamura, et al (1976), which is accurate to within a few percent except near the critical regions. The Poynting correction factor, Φ_{H_2O}, was calculated from a fundamental thermodynamic equation (Prausnitz, 1969), using an equation for the liquid molar volume for water by Roesl (Yaws, 1974)

Correlation of Henry's Law Coefficient

Of course, Henry's law coefficient, H_{CH_4}, in equation (6) was not a priori calculable for methane in water. The available published experimental solubility data had to be used to obtain a correlation of Henry's law coefficient with temperature, pressure, and methane content of the liquid phase. The correlation procedure was: first, compute Henry's law coefficient for each experimental data point using equations (5) and (6), then correlate the resulting experimental coefficients, using a fundamentally-based equation containing parameters to be determined by a non-linear least squares procedure. The final step was to write subroutine SOLUTE, which solves equations (5) and (6) for x_{CH_4} and y_{CH_4} given temperature and pressure, using the Henry's law coefficient equation developed by the correlation procedure.

The equation used to correlate Henry's law coefficient for the methane-water system was:

$$\text{Ln}\,(H^o{}_{CH_4}) = a_o + \frac{a_1}{R_c}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{a_2}{R_c}(T - T_o) + \frac{b}{R_gT}(1+cP)(P) + \frac{d}{R_c}(x^2_{H_2O} - 1) \qquad (7)$$

where, $H^o{}_{CH_4}$ = Henry's law coefficient for methane in water, psi

a_o = Ln H^o at $P=0$, $T=T_o$, $x_{H_2O}=1$

a_1 = partial molar enthalpy of solution for methane in water, cal/g mol, at T_o

a_2 = temperature dependence of a_1, cal/g mol-K^2

b = partial molar volume of methane in water, cc/g mol

c = compressibility of b, atm^{-1}

d = Margules' coefficient for methane in water, cal/g mol-K

T = temperature of system, K

P = pressure of system, atm

x_{H_2O} = mol fraction water in liquid

T_o = reference temperature, 455.7 K

R_c = gas constant, 1.987 cal/g mol-K

R_g = gas constant, 82.05 cc-atm/g mol-K

In equation (7), the dependence of Henry's law coefficent upon temperature, pressure, and liquid composition is expressed in terms of physically meaningful parameters in accordance with fundamental relationships developed in standard thermodynamic textbooks, e.g., Prausnitz, (1969). It was found that the overall fit of this equation to the experimental data could be improved statistically by allowing for temperature dependence of parameters b and d.

The values for these parameters, found by a non-linear least squares fit of the data from the sources in Table 1, are given in Table 2. To arrive at the final parameter values shown in Table 2, a few isolated data points from some of the data sets were excluded based on obvious inconsistencies with the overall trends. In addition, all data for temperatures above 350° C (662°F) were excluded, not because the data were suspect, but because the calculation of methane fugacity coefficients using the Nakamura, et al (1976) equation is not reliable near the critical temperature of water (374.2°C).

Table 2. Values of Parameters for Henry's Law Coefficient Correlation Equation* for Methane-Water System

Parameter	Value	95 Per Cent Conf. Limits
a_o	10.407	± 0.0197
a_1	-6814.8	± 199.9
a_2	-0.0533	± 0.0105
b	$62.33 + 0.007338(T-T_o)$	± 5.79
c	-9.149 E-5	± 3.93 E-5
d	$22.73 - 549.8\ \text{Ln}(T/T_o)$	± 6.85

* See Equation (7) in text

Comparision of Correlations for Methane-Water

The effectiveness of the LSU correlation for representing the experimental data sets (for the methane-water system) is summarized in Table 3, with the results for the correlations of Haas (1979) and Blount (1981) also shown for comparison. Both root mean square (r.m.s.) and average deviations were calculated for the isotherms each data set.

Since the revised Blount equation was recommended only for pressures above 2000 psi and temperatures above 200° F., the deviations for Blount were calculated excluding any data points below these limits. The r.m.s. deviations for the Blount equation were, however, generally larger than for the other two correlations; and the average deviations for the Blount equation were decidedly non-zero, indicating that there remains a discrepancy between the revised Blount data and the other data sets. The revised Blount data set was not available for inclusion in Table 3 at the time this paper was prepared.

For data sets on which the Haas correlation was based (Culperson-McKetta and Sultanov, et al), the Haas correlation gave the smallest average r.m.s. deviation, about 5%, compared to about 8% for the LSU Correlation. But for the remaining data sets the Haas correlation was less effective, resulting in an average r.m.s. deviation of 9.2% for the entire combined data sets, compared to 8% for the LSU correlation.

The largest deviations for the Haas correlation occured in the Price data, where it substantially overestimated the methane solubility for pressures above 10,000 psi. This was probably due to the use of partial pressure instead of fugacity in the correlation. At high pressures, because of the effect of the attractive forces between molecules, the fugacity of a vapor phase component can be substantially below its partial pressure.

In summary, the LSU correlation, which was based on the entire data set, fits the data consistently throughout the range better than the Haas correlation, which was based on a portion of the data set only. The revised Blount equation, which was based on the

Table 3. A comparison of Solubilities of Methane in Water (SCF/B) Calculated by Haas, Blount, and LSU Correlations with Published Data

Data Set	N, No. of Points	t, Temp. Deg. F.	P, Pressure Psia	RMSD, r.m.s. relative dev.**			AD, avg. relative dev.***		
				Haas	Blount*	LSU	Haas	Blount*	LSU
1 Sultanov, et al (1972)	10	302	715 - 15650	.0325	.100	.0628	-.0252	.0694	-.0213
	11	392	711 - 15650	.0777	.0826	.0591	-.0715	.0087	.0539
	11	482	1422- 15650	.0463	.205	.0663	.0046	.0716	.0066
	10	572	2134- 15650	.0540	.416	.0306	-.0038	.147	-.0251
	9	662	2845 - 15650	.0364	1.34	.0715	.0130	.477	-.0584
	9	626	2845 - 15650	.0717	.647	.0600	.0529	.228	-.0162
	6	680	3556 - 11379	.0714	.779	.161	-.0624	.271	-.0963
Total	66	302-680	711 - 15650	.0560	.627	.0748	-.0122	.167	-.0137
2 Culberson-McKetta (1951)	12	77	341 - 9300	.0843	--	.193	.0563	--	.0617
	12	100	330 - 9895	.0201	--	.0570	.0005	--	-.0104
	12	160	331 - 9865	.0227	--	.0249	-.0036	--	.0014
	12	220	333 - 8190	.0257	.124	.0259	.0069	.117	.0126
	12	280	336 - 9835	.0329	.130	.0436	.0153	.118	.0217
	12	340	323 - 9995	.0276	.143	.0413	.0017	.103	.0237
Total	72	77-340	323 - 9995	.0419	.133	.0870	.0129	.113	.0185
3 Price(1979)	8	309	2204 - 23778	.107	.0958	.0884	.0050	.0748	-.0497
	7	403	2323 - 27908	.0525	.0792	.0530	.0153	.0571	-.0215
	6	430	5332 - 20530	.0548	.0620	.0554	.0194	.0017	-.0092
	12	453	2160 - 23837	.0814	.119	.0693	-.0415	-.0218	-.0586
	9	536	2866 - 27393	.208	.181	.107	.179	.118	.101
	7	558	1567 - 24498	.218	.265	.104	.168	.175	.0879
	7	601	3631 - 27746	.275	.152	.097	.185	.0113	.0427
Total	56	309-601	1567 - 27908	.161	.147	.0848	.0734	.0556	.0092
4 O'Sullivan and Smith (1970)	6	125	1470 - 8818	.0251	.130	.0151	-.0181	-.130	.0035
	6	217	1484 - 8876	.0362	.110	.0164	.0081	.106	.0005
	6	257	1514 - 8935	.114	.237	.0953	.0960	.236	.0889
Total	18	125-257	1470 - 8935	.0706	.168	.0565	.0287	.0707	.0310
5 Namiot, et al(1979)	7	122-662	4595	.0465	.286	.0310	-.0099	.150	.0015
TOTAL FOR ALL DATA	219	77-680	711 - 27908	.0930	.414	.0794	.0214	.112	.0069

* r.m.s and avg. deviations for revised equation of Blount (1981) excluded data points for temperatures less than 200 °F and pressures less than 2000 psia

** $$\text{RMSD} = \left\{ \sum^{N} \left[\frac{(SCF/B_{calc} - SCF/B_{exp})^2}{(SCF/B_{exp})^2} \right] \Big/ N \right\}^{1/2}$$

*** $$\text{AD} = \sum^{N} \left[\frac{(SCF/B_{calc} - SCF/B_{exp})}{(SCF/B_{exp})} \right] \Big/ N$$

revised Blount data (not available until July, 1981), did not represent these data sets as well as the other two correlations, indicating a bias or discrepancy may still exist.

The fact that the LSU correlation did not fit the data sets used for the Haas correlation as well as did the Haas correlation suggest there are some inconsistencies (biases) between the various data sets which prevented the "global" fit from being as effective as was desired.

Correlation of Salting-Out Coeffieient

Calculation of Experimental Salting-Out Coefficients

Since NaCl acts as a non-volatile component when it is present in the liquid phase, it is not useful to write equilibrium equations such as equations (3)-(6) for the salt component. To account for the effect of NaCl upon methane solubility, the semi-empirical Sechenov (salting-out) coefficient, K_s, is used:

$$\text{Log}_{10}(x_{CH_4}/x^{o}_{CH_4}) = -mK_s \qquad (8)$$

where the ratio on the left-hand side is the methane dissolved in a salt solution divided by that in pure water at the same conditions, and m is the molality (g mols salt/1000 g water) of the methane-free liquid.

It was reasoned that the above equation actually reflects the effect of the NaCl upon the fugacity of the methane in the liquid, as measured by Henry's law coefficient. Accordingly, equation (8) was replaced by:

$$\text{Log}_{10}(H_{CH_4}/H^{o}_{CH_4}) = mK_s \qquad (9)$$

In equation (9) the negative sign has disappeared because methane dissolved is inversely proportional to Henry's law coefficent.

To correlate the experimental data for salt solutions, experimental values for Henry's law coefficient were calculated, as before, for each data point; then experimental values for the salting-out coefficient, K_s, were calculated from equation (9). The experimental salting-out coefficients thus obtained were empirically correlated vs. temperature, pressure, and salt molality.

Correlation of the Salting-out Coefficient The extensive Blount data comprise the bulk of the published data for the mathane-water-salt system. The Namiot data, though limited to only one concentration of salt, are valuable because of the upper temperature range investigated.

Although the original Blount data were not used in developing the Henry's law coefficient correlation for methane-water, it was hoped that salting-out coefficients calculated with the Blount data might be consistent with those calculated from other sources, due to the cancelling out of a common bias. Accordingly, an empirical regression was performed using a data set which included the salting-out coefficients for the Blount data. No effect of pressure or salt molality was found on the salting-out coefficient, but a strong temperature dependence was identified. This temperature effect can be seen in Figure 1, in which the experimental salting-out coefficients (average over pressure) are plotted versus temperature. Also plotted is the curve which resulted from the least-squares regression. The equation for this empirical regression curve is:

$$K_s = K_o + K_1(T-T_o) + K_2(T-T_o)^2 \qquad (10)$$

The parameters and their 95% confidence limits were determined:

K_o = 0.08 ±.00973
K_1 = 0.0002751 ±.0000653
K_2 = 4.39 E-6 ±1.59 E-6
T_o = 455.65 °C (arbitrary ref. temp.)

This results in a minimum value for K_s of 0.076 at 151°C. From Figure 1 it can be seen that the shape of the regression curve was dictated primarily by the high temperature data of Namiot, coupled with the Blount data in the mid-range of temperature. Were the three high temperature Namiot data points excluded, a very different curve would have resulted. In addition, when each of the data sources is examined separately, there is no observable temperature dependence for temperatures below 200°C.

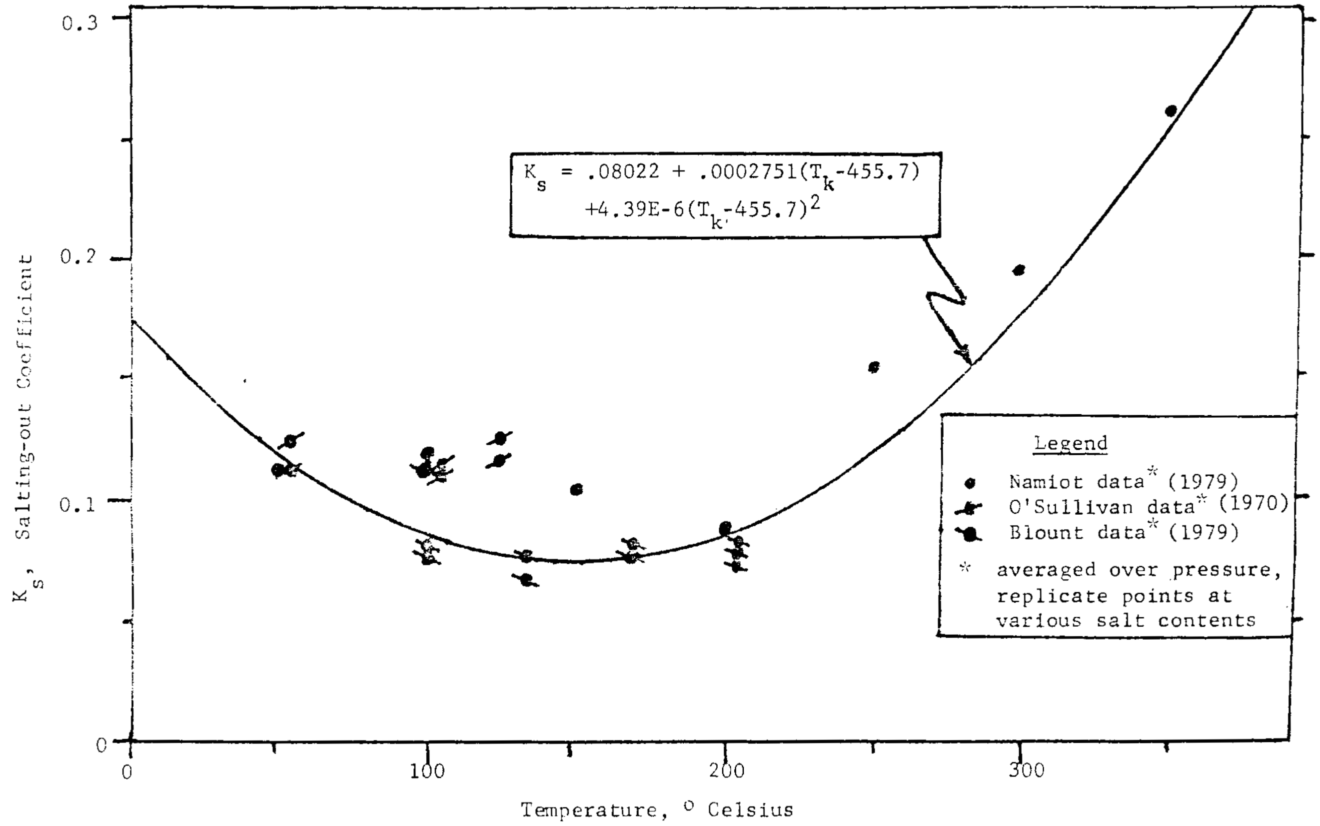

Figure 1. Correlation of Salting-out Coefficient with Temperature for Methane-Water-NaCl system

Finally, were the Blount data excluded, the salting-out coefficient would probably be represented by a constant value of about 0.11 (as previously suggested) up to about 200°C., followed by an upward slope above 200°C. required to fit the high temperature Namiot data points.

Because of the uncertainty connected with the Blount data, the question concerning the best relationship for the salting-out coefficient remains unresolved at the time this paper is written. If possible, an addendum to this paper will be prepared for distribution at the conference to include the effect of the revised Blount data on the results presented here.

CONCLUSIONS

- A new correlation of the available published data for the solubility of methane in water, excluding the data of Blount (1979), was developed, based on fundamental thermodynamic relationships.
- The new correlation represents the entire data set more consistently, with a slightly lower r.m.s. deviation, than the Haas correlation.
- Because the Haas correlation represents the Culberson-McKetta and Sultanov, et al data sets better than the new correlation, there is reason to suspect that some biases exist amoung the various data sets which prevented achievement of a better overall correlation.
- An empirical relationship for the salting-out coefficient as a function of temperature was determined including the original data of Blount (1979) in the data set. This relationship exhibits a strong temperature effect, resulting in a minimum value of 0.076 at a temperature of 151°C.
- Because of the uncertainty connected with the original Blount data, the results reported here are not as definitive as otherwise would have been expected.

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THIS WORK WAS FUNDED BY THE U.S. DEPARTMENT OF ENERGY. CONTRACT NO. DE-AS05-78ET27160