

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THE SOLUBILITY OF METHANE IN
SODIUM CHLORIDE BRINES

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Open-File Report 81-1294

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1981

ABSTRACT

The solubility of methane in pure water and in solutions of 5%, 10%, 15%, and 20% (by weight) sodium chloride was determined experimentally at various temperatures and pressures. Methane solubility in sodium chloride solutions is significantly less than it is in pure water because of the salting-out effect. For example, in a solution of 20 weight % NaCl, the solubility of methane is only 28% of that in pure water under the same temperature and pressure conditions. We report here an experimentally determined value of 0.129 ± 0.03 for the salting-out (Setschenow) constant for methane. Also presented is a set of equations for calculating the solubility of methane under conditions of pressure, temperature and salinity as great as 137.9 MPa (20,000 psi), 350°C (662°F) and 25 weight % sodium chloride, respectively when only the salting-out constant and the solubility of methane in pure water at the temperature and pressure of interest are known.

INTRODUCTION

In the northern Gulf of Mexico sedimentary basin, large regions are distinguished by highly saline pore waters at unusually high temperatures and pressures (Kharaka and others 1977). These regions, known as geopressured-geothermal zones, underlie vast areas of coastal Texas and Louisiana along the Continental Shelf and are known to contain dissolved natural gas, primarily methane (Papadopulos and others, 1975). Pressure, temperature, and salinity in these subsurface waters can reach nearly 124.1 MPa (18,000 psi), 200°C (392°F) and 275,000 mg/L, respectively (Kharaka and others, 1978). Knowledge of the chemical behavior of methane in aqueous solution under these conditions is therefore of the utmost importance if estimates of the energy content of the dissolved gas in these geopressured-geothermal reservoirs are to have maximum reliability. Existing data on the solubility of methane at conditions approximating those in the geopressured-geothermal zones are limited and cover rather narrow temperature, pressure, and salinity ranges. The present investigation was undertaken in order to gather enough experimental data to derive a set of equations that will accurately predict methane solubility in pure water and brines of as much as 25 weight % NaCl at temperatures as high as 350°C (662°F) and pressures as great as 137.9 MPa (20,000 psi).

EXPERIMENTAL METHOD

The experimental apparatus (figure 1) consists of two 6 inch-long gold-lined pressure vessels of known volume, each fitted with a titanium plunger and connected by a titanium capillary tube to a valve assembly. The valve assembly consists of two stainless steel miniature valves and a Setra Model 204 pressure transducer. The temperature of each pressure vessel was measured by a type T thermocouple and a digital voltmeter. Pressure was displayed by a Setra Model 300A digital pressure readout. In addition, both temperature and pressure were continuously monitored on a strip-chart recorder. For each run, the pressure vessels were placed inside a mechanical convection oven and evacuated overnight to 1.33 Pascals. The pressure transducer was then adjusted for the correct reading on the digital readout.

A 150-cc stainless steel gas transfer bottle filled with Matheson Purity methane (99.99%) was weighed and then connected to the entry valve. The gas was admitted to the pressure vessel until the pressure was 0.37 MPa. (0.37 MPa represents the ideal gas pressure for 0.07 gm. CH_4 and is used so that pressure will not exceed the limits of the pressure transducer after the temperature is increased.) The bottle was then removed and reweighed, and the amount of methane added was then calculated by the weight difference (generally about 0.0600 to 0.0800 gm). The brine solution was prepared from a weighed amount of reagent-grade sodium chloride and a weighed amount of deionized water which had been degassed by boiling under a vacuum for 3-4 hours and rapidly cooled. The sodium chloride solution was transferred to a graduated cylinder and weighed. The volume of solution needed was calculated from the volume needed to fill the pressure vessel at 300°C (572°F) and 68.9 MPa (10,000 psi) using the density tables of Potter and Brown (1977). This volume was transferred to the pressure vessel by means of a screw pump pressure

generator. The graduated cylinder was then reweighed, and the weight of solution added was determined by difference. The oven was then turned on and the temperature was increased in steps, the resulting pressures being recorded at each step. The runs were allowed to equilibrate for a minimum of 3 hours (usually longer) at each temperature interval. The temperature was increased in increments until the volume of the liquid expanded to fill the vessels completely. This is shown graphically by line AB in figure 2. The temperature increases were then continued in small steps to determine the P-T curve for the liquid at constant volume (ignoring dv/dt for the pressure vessel) and composition until the pressure limits of the equipment were reached (nominally 68.9 MPa [10,000 psi]). This is shown graphically by line BC in figure 2. As a check, the temperature was then decreased in small increments, with the resulting pressure being recorded at each interval, until room temperature was again reached.

Lines AB and BC in figure 2 depict two intersecting curves representing two-phase (liquid-vapor) and one-phase (liquid) conditions respectively. By using a curve-fitting routine on the experimental data, the function $(dp/dt_{x,v})$ can be derived for each of the curves. Those functions are in turn used to calculate the intersection temperature and pressure for the two curves. These results, along with the fixed values for volume and composition, are used to calculate the methane solubility. The experimental results are shown in table 1.

METHANE SOLUBILITY IN PURE WATER

The solubility of methane in pure water has been measured previously by various investigators (Culberson and McKetta, 1951; Duffy and others, 1961; O'Sullivan and Smith 1970; Sultanov and others, 1972; and Price 1979). The data from those studies and the present study were evaluated in several different ways in order to derive the simplest algebraic function to describe the data. Of the correlations tried we found that only the plots of $\log Q$ versus x_{CH_4} were linear for several isotherms over the entire pressure range. Q is defined here by the equation,

$$Q = \frac{x_{CH_4}}{p_{CH_4}} \quad (1)$$

where x_{CH_4} is the molal concentration of methane in water and p_{CH_4} is derived by subtracting the vapor pressure of pure water at the temperature of interest from the total pressure. The logarithm of Q is written as

$$\log Q = \log x_{CH_4} - \log p_{CH_4} \quad (2)$$

The data from the present investigation and most of the previously mentioned investigations are in good agreement. By using these data each isotherm was fit to the function.

$$\log Q = a + bx_{CH_4} \quad (3)$$

The intercept (a) and the slope (b) were derived by using the technique of Haas (1978). These two variables were then each fitted to polynomials in temperature ($^{\circ}C$) the reciprocal of the variances at each isotherm being used to weight the data. The data of Price (1979) were not included in the calculation of a and b because when his data were used, plots of $\log Q$ versus the molality of methane did not yield linear results.

The following equations were derived for the intercept and the slope of equation 3:

$$a = -4.3345 \times 10^2 t^{-2} + 35.7727 t^{-1} - 3.56262 + 2.19921 \times 10^{-5} t^2 - 2.68155 \times 10^{-8} t^3 \quad (4)$$

$$b = 40.3932 t^{-1} - 4.04655 + 2.85046 \times 10^{-2} t - 7.08934 \times 10^{-5} t^2 + 6.14288 \times 10^{-8} t^3 \quad (5)$$

where t is in degrees Celsius ($^{\circ}\text{C}$).

The estimated partial pressure of methane in the system is the difference between the total pressure and the partial pressure of water at the temperature under consideration.

$$P_{\text{CH}_4} = P_{\text{total}} - P_{\text{H}_2\text{O}} \quad (6)$$

Combining equations 2, 3, and 6 and rearranging terms results in the expression:

$$\log(P_{\text{total}} - P_{\text{H}_2\text{O}}) = -a - b x_{\text{CH}_4} + \log x_{\text{CH}_4} \quad (7)$$

The partial pressure of water can be derived from data in Haas (1976). When those values for $P_{\text{H}_2\text{O}}$ are used along with the total pressure, the solubility of methane in pure water can be computed from equation 7. Values for the solubility of methane in water calculated in this manner are plotted in figure 3.

METHANE SOLUBILITY IN SODIUM CHLORIDE SOLUTIONS

Several investigators in the past have pointed out that the solubility of nonpolar gases in aqueous electrolyte solutions decreases with increasing electrolyte concentration because of the salting-out effect (Morrison and Billett, 1952 Namiot, 1961). The relationship between the solubility of a gas like methane in pure water versus its solubility in an electrolyte solution can be quantitatively expressed as a Setschenow type-equation,

$$\log y_{\text{CH}_4} = \log x_{\text{CH}_4} - A_S I \quad (8)$$

where y_{CH_4} is the molal solubility of methane in the electrolyte solution, x_{CH_4} is the molal solubility of methane in pure water at the same temperature and pressure A_S is the Setschenow (or salting-out) constant, and I is the ionic strength of the solution. Although the true ionic strength of the electrolyte solution will be less at higher temperatures owing to increased association of NaCl precise evaluations of the influence of temperature of ionic strength are beyond the scope of this report. Therefore I , is arbitrarily set to equal the molality of sodium chloride.

To evaluate the Setschenow constant, equation 8 is rearranged to read

$$A_S = \log \left(\frac{x_{\text{CH}_4}}{y_{\text{CH}_4}} \right) / I \quad (9)$$

Thus, for experimental runs in aqueous sodium chloride solutions, the molality of methane and the molality of NaCl are determined from the starting conditions. The temperature and pressure at the intersection point (B on figure 2) are determined from the experiment, and a value for the solubility of methane in pure water at this same intersection temperature and pressure is then used for x_{CH_4} in equation 9.

The value for the Setschenow constant determined from this investigation is 0.129 ± 0.030 . The major source of uncertainty for A_S is the determination of the pressure value for the intersection point (B) on the liquid-vapor curve. As line BC (figure 2) is relatively steep, small temperature changes result in large pressure changes, so that it is difficult to resolve the pressure precisely. The calculated value for A_S is also sensitive to the value used for the solubility of methane in pure water in equation 9. However, that value, as mentioned previously is based upon the present investigation in combination with several previous investigations, all in good agreement, so that the error contribution from x_{CH_4} is considered insignificant. Finally, we tested the variation of the Setschenow constant as a function of temperature, weight % NaCl, molality of methane, and pressure, using multiple-regression analysis, and we found that A_S could not be correlated with changes in any of these variables over the range of experimental conditions. Indeed it is probably too simplistic an approach to try to correlate A_S with any one variable because of the complex influence of many factors on intermolecular interactions within the sodium chloride solutions.

Once A_S is known the solubility of methane in aqueous salt solutions at a variety of temperature and pressure conditions can be calculated from equation 8, when only the solubility of methane in pure water under the same conditions is known. A routine based on this equation for calculating methane solubility in pure water or NaCl brines that make use of a programmable hand calculator has been described previously (Susak and McGee, 1980).

RESULTS

Smoothed values for methane solubility are presented in several different ways. Figures 4 through 7 are semilogarithmic plots of methane solubility as a function of temperature at several fixed salinity values. Pressures of 6.9 MPa (1,000 psi) to 137.9 MPa (20,000 psi) are shown as contours. These figures show that increasing pressure results in an increase in methane solubility. Increasing the temperature also increases methane solubility except at low pressures. At low total pressures, the vapor pressure of water increases significantly as temperature increases, resulting in a corresponding decrease in the partial pressure of methane. As the vapor pressure of water approaches the total pressure in the system, the solubility of the gas approaches zero.

Figures 8 and 9 are semilogarithmic plots showing methane solubility as a function of temperature at fixed pressures of 6.9 MPa (10,000 psi) and 137.9 MPa (20,000 psi), respectively. Salinity values from 0% to 20% sodium chloride are shown as contours. Both these plots clearly illustrate the effect of the salting-out process on methane solubility. As the concentration of sodium chloride electrolyte is increased, the solubility of methane is reduced.

Published values for the solubility of methane in sodium chloride solutions at temperatures of geologic interest are scarce. O'Sullivan and Smith (1970) reported data on the solubility and partial molar volume of methane in salt solutions at isotherms of 51.5°C, 102.5°C, and 125.0°C over the pressure range 10.1 to 60.8 MPa (1465 to 8818 psi). Figure 10 shows a comparison between the smoothed solubility values of the present study and the experimental data points (recalculated to molality) of O'Sullivan and Smith at 125°C. Methane molality is plotted as a function of pressure

of the gas) in the system. Clearly the salting-out process is very complex.

Regardless of the mechanism, the data presented herein demonstrate the large effect that salting-out has on the solubility of methane in sodium chloride brines. At any given temperature and pressure, the solubility of methane in 10 weight % NaCl solutions is only 57% of that in pure water. At 20 weight % NaCl, the amount of dissolved methane is further reduced to only 28% of that in pure water at the same temperature and pressure. Figure 12 summarizes the effect of the NaCl electrolyte on the solubility of methane. From the evidence presented in this report, any estimate of methane content in geopressured-geothermal zones clearly must take into account the effect of the salting-out phenomenon on the solubility of methane. We hope that the data presented herein can be used as a guide to that end.

with contours of 0 m, 1 m, and 4 m NaCl. The average variation between the two studies is about 7.5 percent. The agreement between the two studies at the 51.5°C and 102.5°C isotherms is similar.

During analysis of the experimental data, we noted that variations in dp/dt did not correlate in any recognizable way either with variations in the molality of methane or with the intersection pressure. There is, however, a moderate correlation of dp/dt with the temperature of intersection (point B on figure 2). The following empirical relationship has been derived

$$dp/dt = 2.842 \times 10^2 - 0.412t \quad (10)$$

where t is the temperature of intersection in °C and the pressure is in terms of psia. The standard error of estimate is 7.1.

DISCUSSION

Experimental measurements of the solubility of methane in sodium chloride solutions clearly demonstrate that the solubility is lowered as NaCl concentration increases. This effect called salting-out, is typically observed for many gases dissolved in electrolyte solutions. In contrast the solubility of a gas can be increased in the presence of certain salts. This effect (salting-in) has been reported for methane in various concentrations of tetraalkylammonium salt solutions (Wen and Hung, 1970; Blanco and Smith, 1978). In either case the salting effect can be conveniently expressed as a function of electrolyte concentration by the empirical Setschenow equation

$$\log(S^{\circ}/S) = A_S I \quad (11)$$

where S° is the gas solubility in pure water, S is the gas solubility in electrolyte solution, and I is the concentration of the electrolyte solution. A_S , the salting coefficient has a positive sign for salting-out and a negative sign for salting-in. Figure 11 shows a plot of $\log (S^{\circ}/S)$ versus weight % NaCl, using data for methane from the present study. The position of the curve above the zero line indicates a salting-out condition.

Morrison and Billett (1952) and O'Sullivan and Smith (1970) reported a variation in the salting-out constant for methane in aqueous sodium chloride solutions as a function of temperature. Both investigations, however, were conducted over a narrow low-temperature range and are therefore only marginally comparable with the present study. The experimental data reported here do not indicate any significant variation of A_S with temperature. O'Sullivan and Smith (1970) also reported a decrease in the value of the salting-out constant for methane when NaCl concentration increased (from 0.125 in 1 m to 0.117 in 4 m NaCl at 125°C). The data from the present study roughly show a similar

trend: however the scatter is such that no relationship between the two can be derived that would result in a significant correlation coefficient. One reason for the uncertain correlation of A_S with salinity or temperature may be that at higher temperatures the dielectric constant of water decreases causing increased association of sodium chloride, which in turn results in smaller true ionic strengths for the electrolyte solutions. It seems quite evident that some incompletely understood complex factors influence the salting-out phenomenon, especially at higher temperatures.

Long and McDevit (1952), Conway and others (1964), and Ruetschi and Amlie (1966) have summarized the major theories previously published to explain salting-out. Basically these theories involve either dielectric effects, compression of the solvent molecules, or hydration of the electrolyte ions. In simplest terms, the hydration theory predicts a reduction in the normal solvent function of water molecules attached to the ions of the electrolyte solution so that the gas effectively has less water in which to dissolve. According to Ruetschi and Amlie (1966), the hydration theory best describes their results on the solubility of hydrogen gas in electrolyte solutions.

One of the problems in formulating a salting-out mechanism valid for a wide range of conditions is that data for nonpolar gas solubility in electrolyte solutions at higher temperatures are scarce. Malinin (1979) has recently suggested that the salting-out phenomenon is influenced by different mechanisms at different conditions and that existing explanations for salting-out are only valid at low temperatures. Malinin (1979) has proposed that any interpretations of the salting-out effect must take into account the influence of three variables: the electrolyte concentration, the concentration of dissolved gas, and the pressure (related to changes in partial molar volume

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Table 1. Summary of individual run data for CH₄

Run No	Wt.% NaCl	Temp. (°C) ^a	Pressure (MPa) ^a	Methane Molality ($\frac{\text{moles}}{\text{Kg}}$)	A _S ^b
1	0	272.6	11.80	0.22648	-
2	0	266.6	10.24	.18621	-
3	0	267.9	10.60	.18621	-
4	0	265.8	10.30	.18621	-
5	0	192.6	12.36	.14984	-
6	0	191.8	11.42	.14984	-
7	0	191.6	11.35	.14984	-
8	5.062	273.5	11.76	.17281	.1682
9	5.062	274.7	11.95	.17281	.1817
10	5.062	272.4	11.02	.17281	.1107
11	5.062	212.9	16.02	.14748	.1891
12	5.062	211.5	13.12	.14748	.0911
13	5.062	211.6	13.34	.14748	.0992
14	10.052	257.8	12.84	.17672	.1042
15	10.060	285.3	13.97	.15832	.1384
16	10.060	288.1	14.22	.15832	.1224
17	10.060	292.3	13.34	.15832	.1305
18	10.060	263.6	13.91	.16906	.1708
19	10.060	265.2	13.49	.16906	.1458
20	10.060	264.1	13.20	.16906	.1782
21	15.1163	285.9	15.52	.16454	.1279
22	15.1163	242.3	16.55	.16137	.1001
23	15.1163	248.1	15.37	.16137	.0958
24	15.1163	248.3	15.24	.16137	.0945
25	20.0000	283.7	16.38	.14843	.1094
26	20.0000	287.1	16.71	.14843	.1140
27	20.0000	285.6	16.70	.14843	.1134
28	20.0000	284.1	17.98	.14218	.1279
29	20.0000	283.7	17.70	.14218	.1254
30	20.0000	283.2	17.68	.14218	.1249

^aThe values for temperature and pressure define the intersection of lines AB and BC in figure 2.

^bA_S is the calculated value for the Setschenow constant for each run.

Figure 1.--Schematic diagram of the experimental apparatus used in this study.

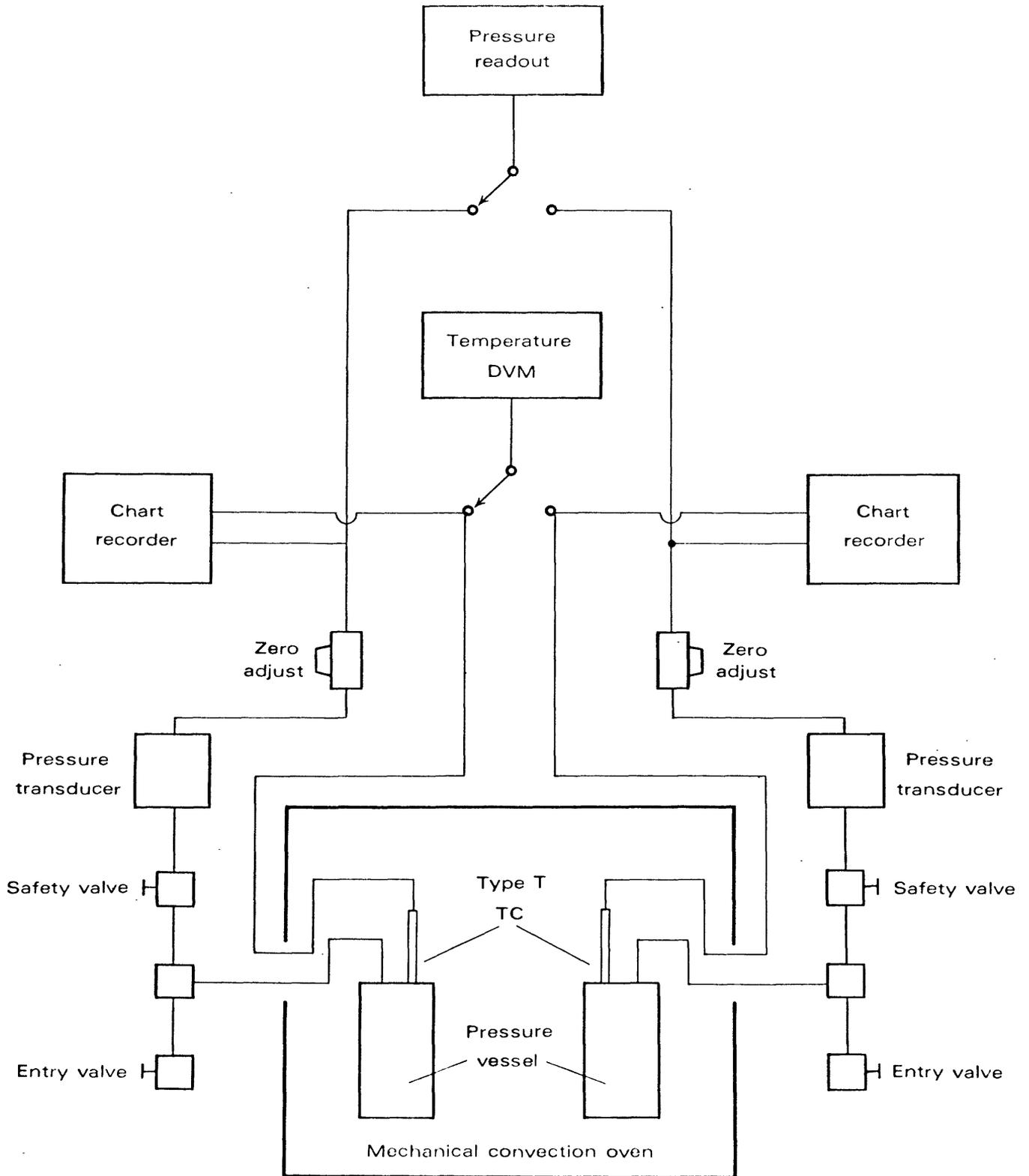


Figure 2.--Schematic P-T plot. Line AB represents the liquid-vapor curve. Line BC represents one-phase (liquid) conditions. B is the point at which the volume of the liquid has expanded to fill the reaction vessel completely.

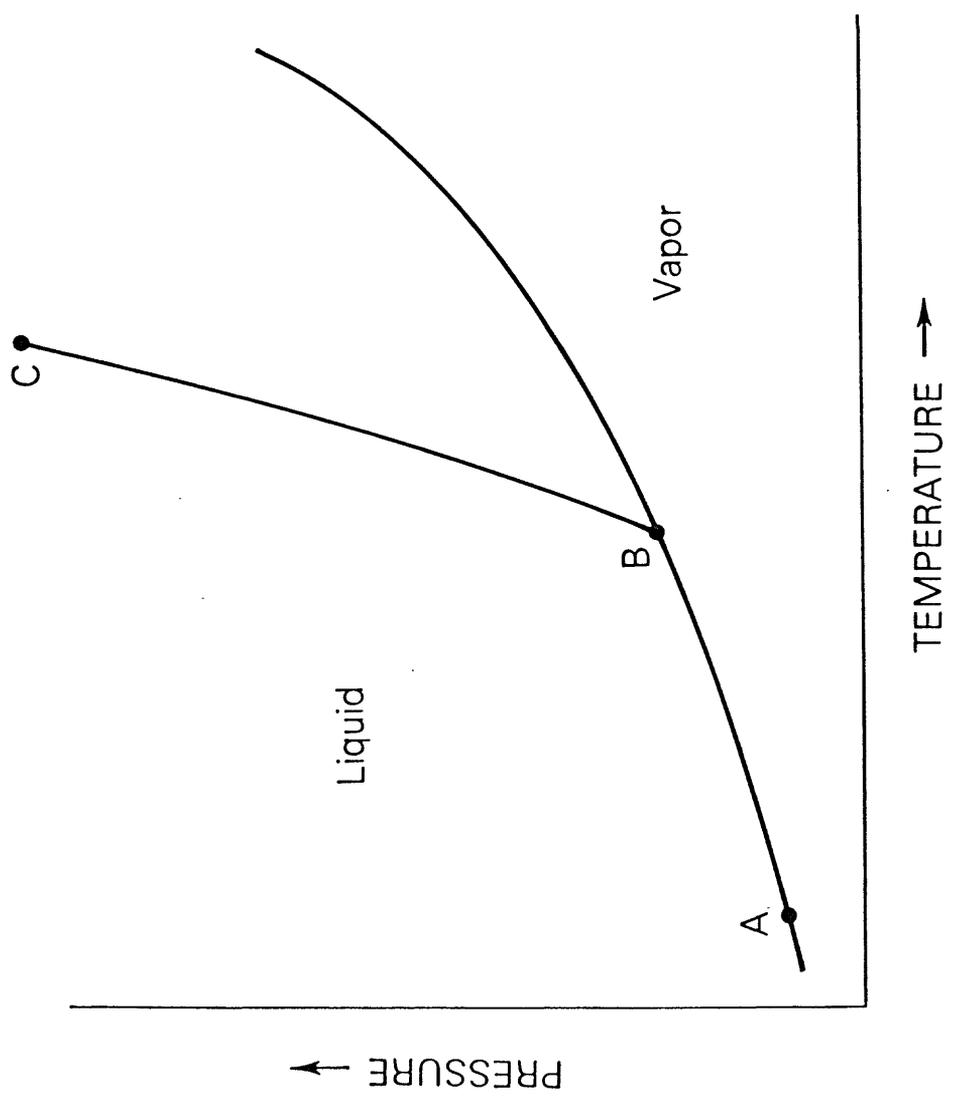


Figure 3.--The solubility of methane in pure water as a function of temperature. The solid curves are pressure isobars from 6.9 MPa (1,000 psi) to 137.9 MPa (20,000 psi). The decline in gas solubility at low total pressures and high temperatures is due to a significant increase in the vapor pressure of water under these conditions resulting in a corresponding decrease in the partial pressure of methane. The quantity standard cubic feet (SCF), is referenced to 15.6°C (60°F) and 0.1 MPa (1 atmosphere). One barrel (bbl) = 42 gallons = 158.98 liters. The following relationship is used to convert methane solubility from molality units to standard cubic feet per barrel: $SCF/bbl = (\underline{m}) (\text{density}) (133.012)$. Pressure in psi = MPa x 145.038.

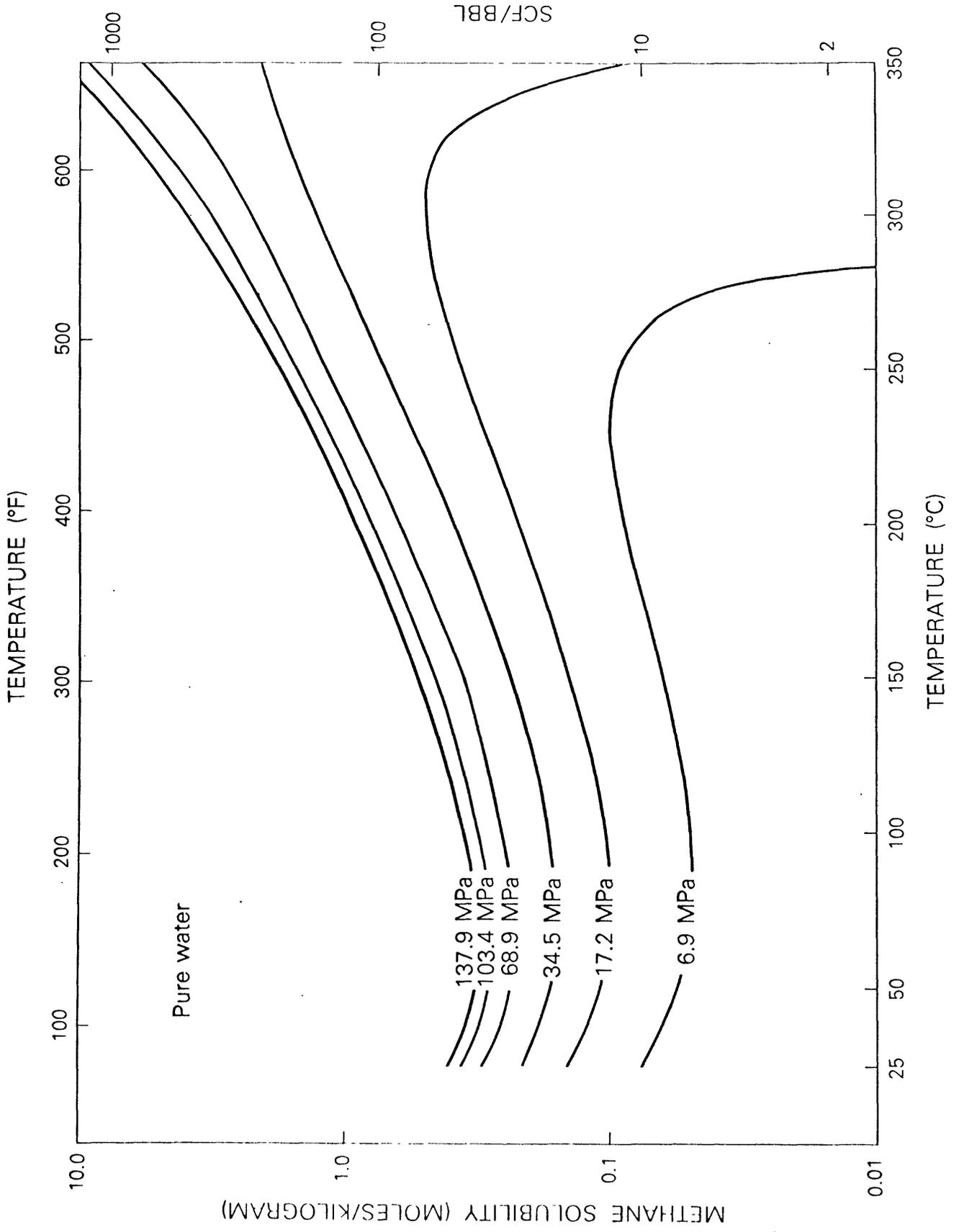


Figure 4.--The solubility of methane in 5 weight % NaCl solutions as a function of temperature. The solid curves are pressure isobars from 6.9 MPa (1,000 psi) to 137.9 MPa (20,000 psi).

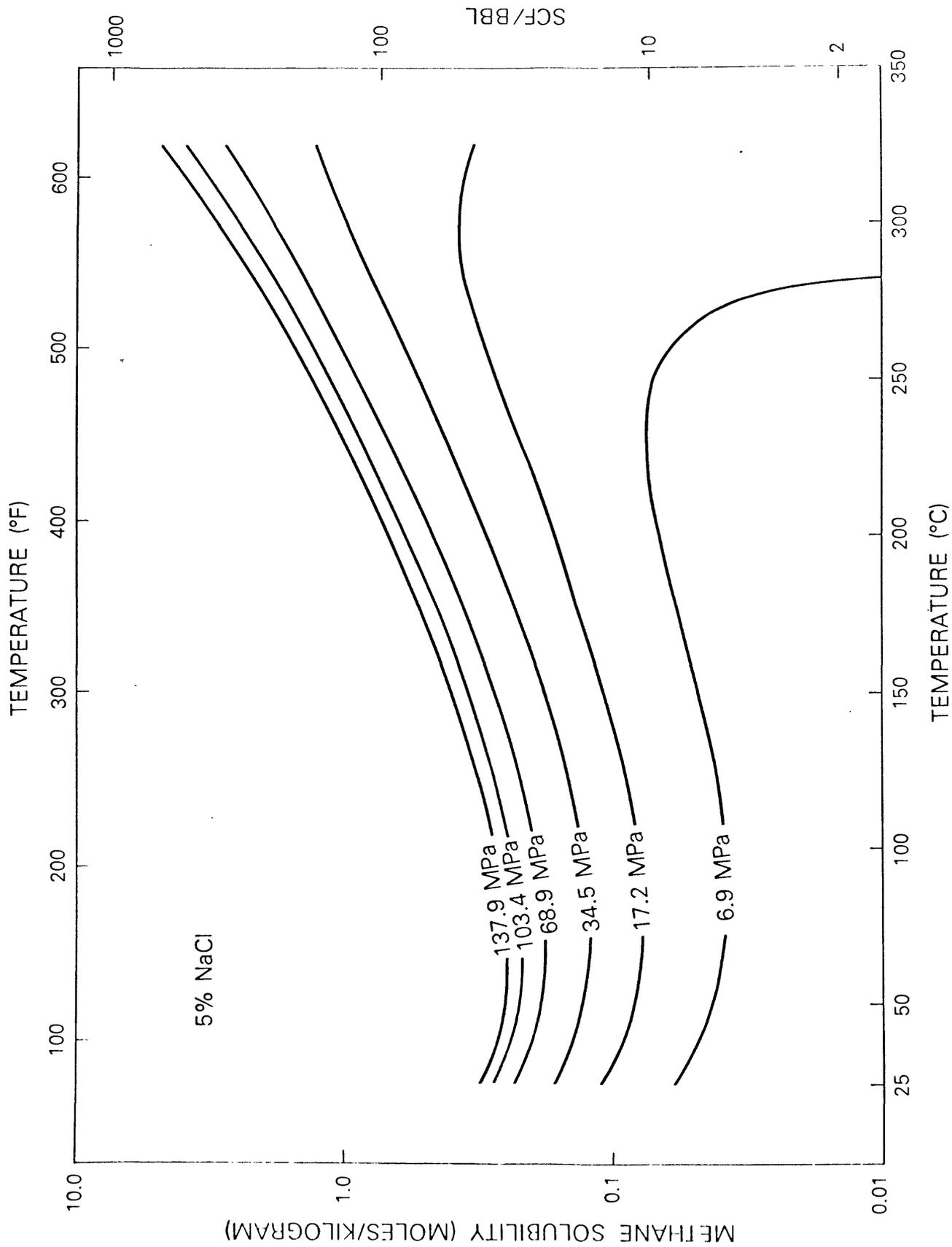


Figure 5.--The solubility of methane in 10 weight % NaCl solutions as a function of temperature. The solid curves are pressure isobars from 6.9 MPa (1 000 psi) to 137.9 MPa (20,000 psi).

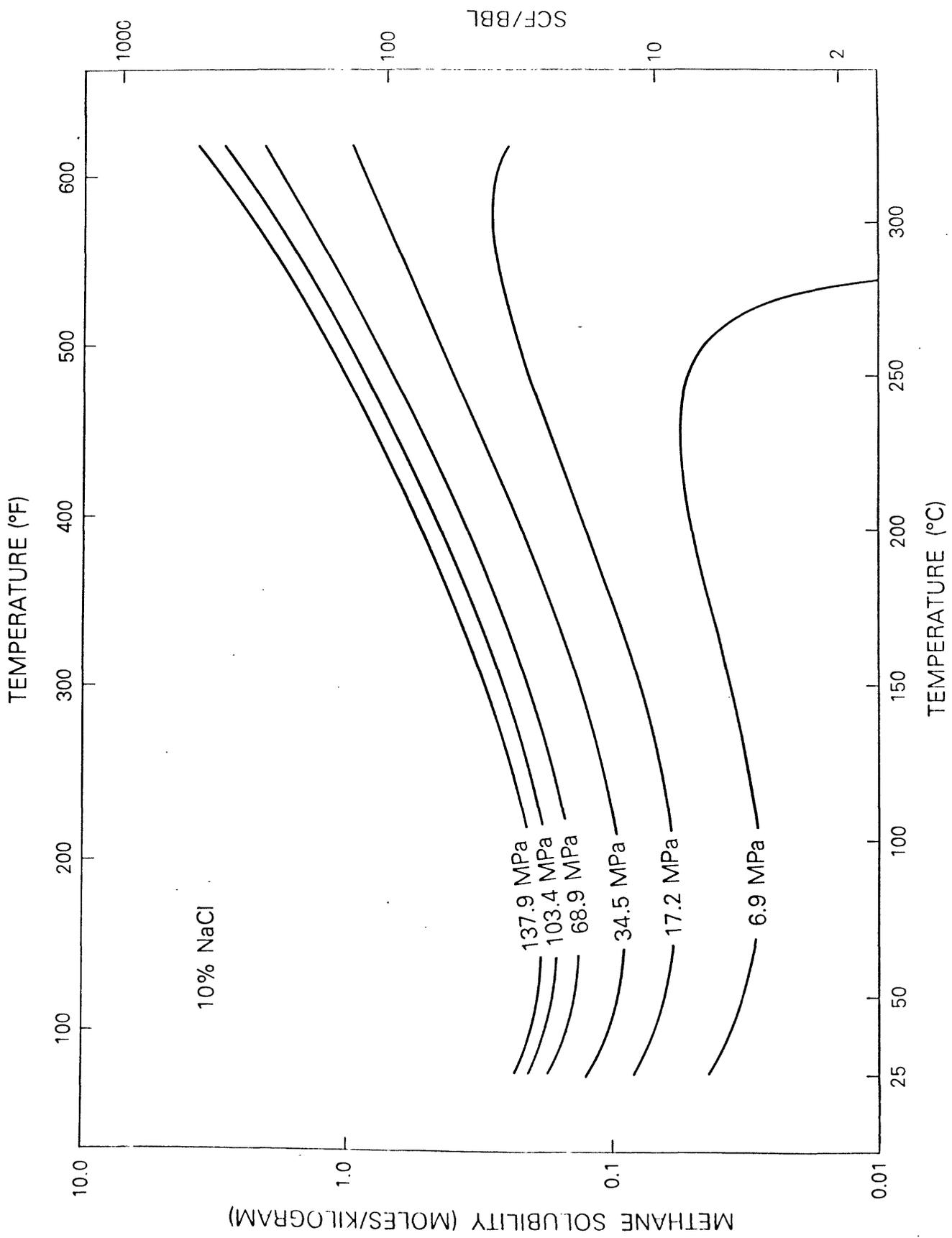


Figure 6.--The solubility of methane in 15 weight % NaCl solutions as a function of temperature. The solid curves are pressure isobars from 6.9 MPa (1 000 psi) to 137.9 MPa (20,000 psi).

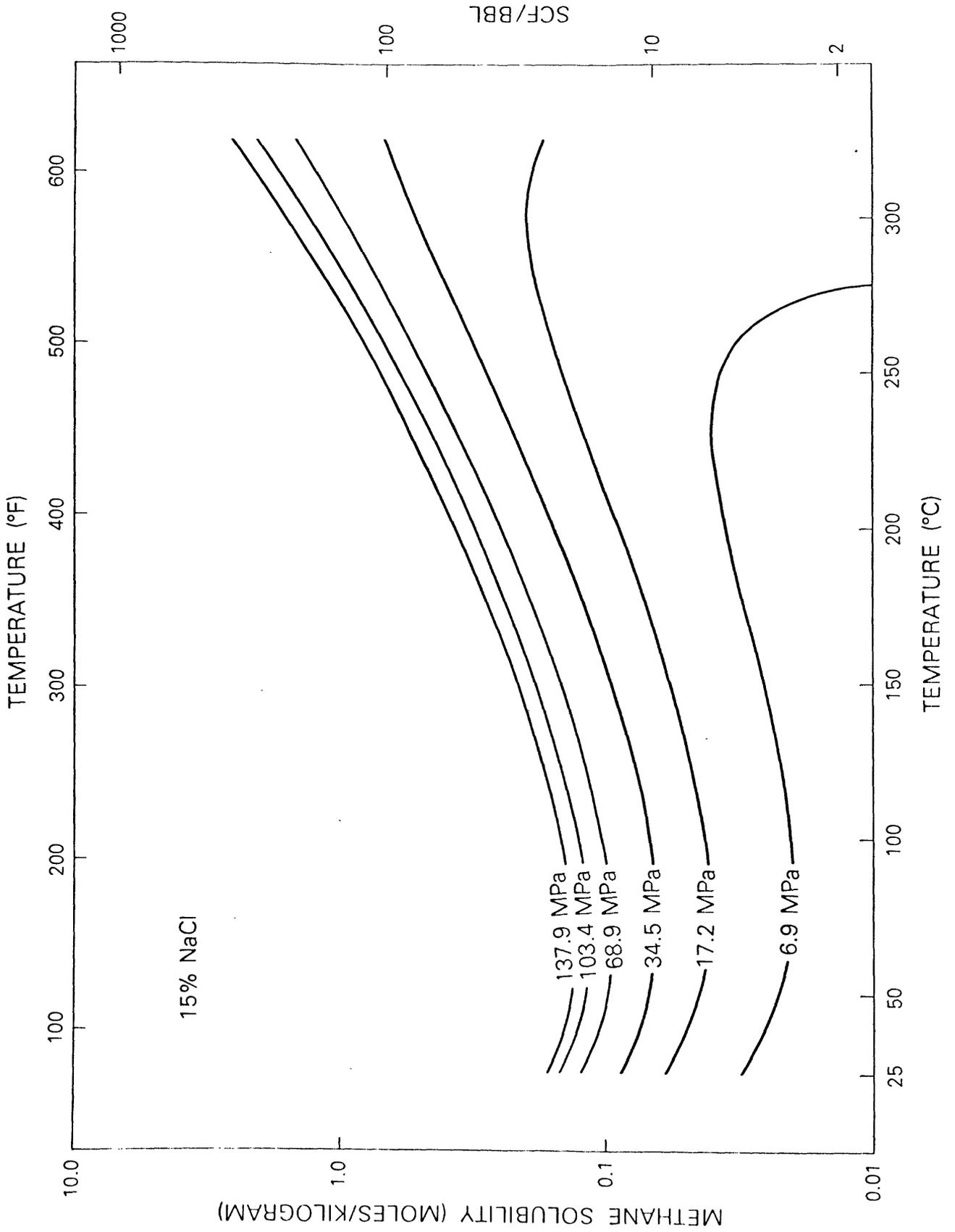


Figure 7.--The solubility of methane in 20 weight % NaCl solutions as a function of temperature. The solid curves are pressure isobars from 6.9 MPa (1 000 psi) to 137.9 MPa (20 000 psi).

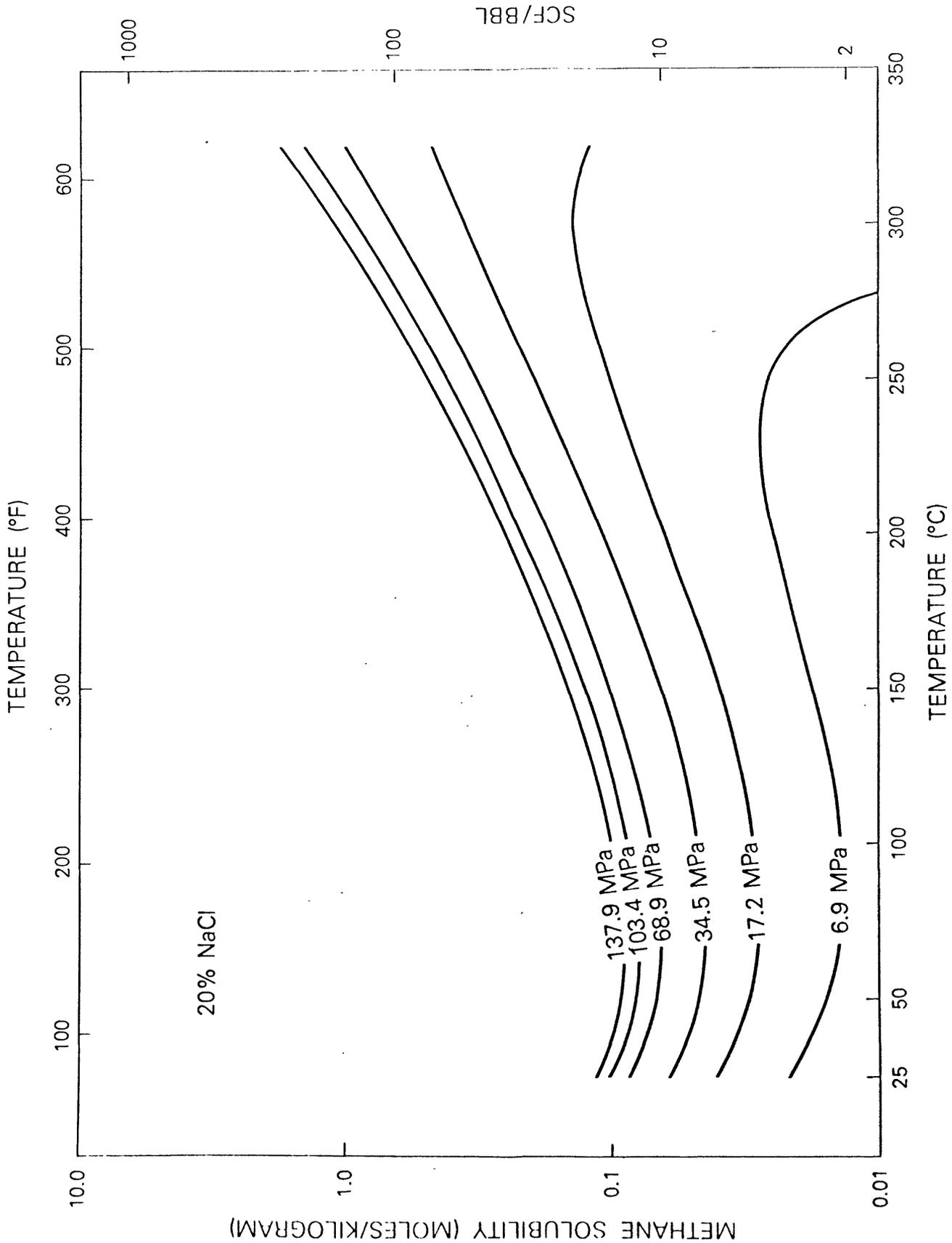


Figure 8.--The solubility of methane at 68.9 MPa (10,000 psi) as a function of temperature. Solid curves are salinity contours from 0% to 20% NaCl. The SCF/bbl scale is approximate because it is a function of the density of the solution.

METHANE SOLUBILITY (MOLES/KILOGRAM)

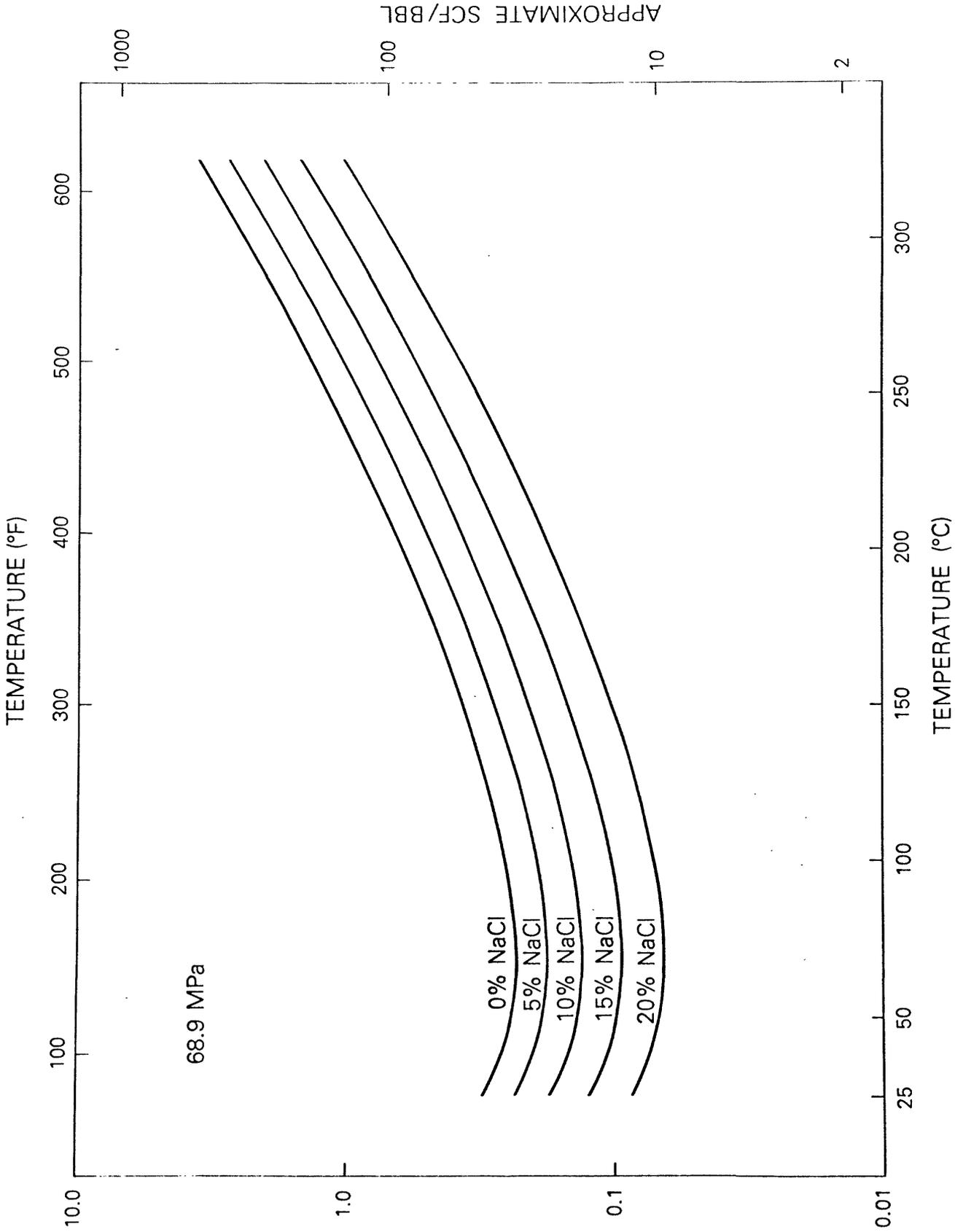


Figure 9.--The solubility of methane at 137.9 MPa (20,000 psi) as a function of temperature. Solid curves are salinity contours from 0% to 20% NaCl. The SCF/bbl scale is approximate because it is a function of the density of the solution.

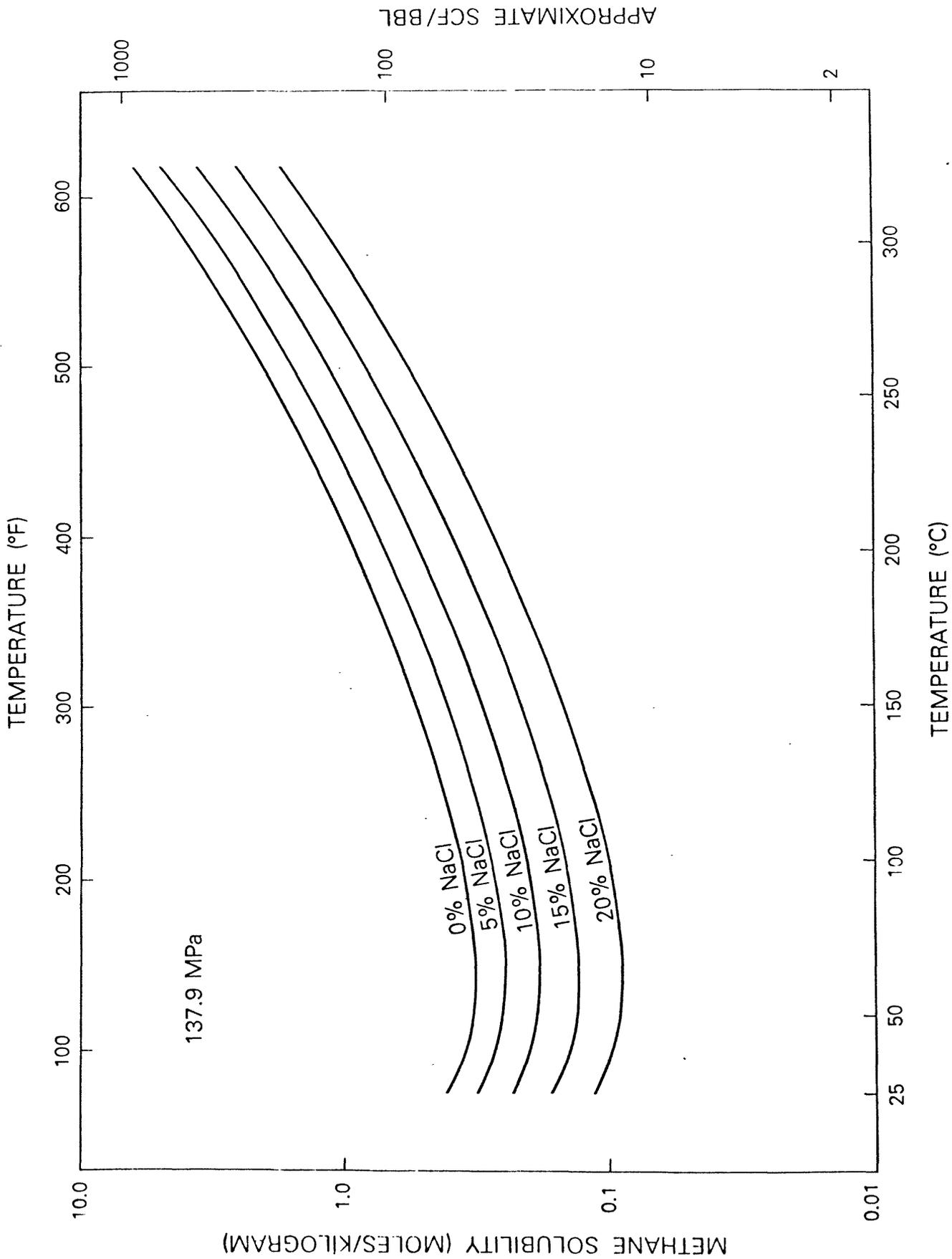


Figure 10.--The solubility of methane at 125°C as a function of pressure.

The solid curves represent smoothed values for methane solubility at 0 m, 1 m, and 4 m NaCl solutions from the present study. The crosses represent data from O'Sullivan and Smith (1970).

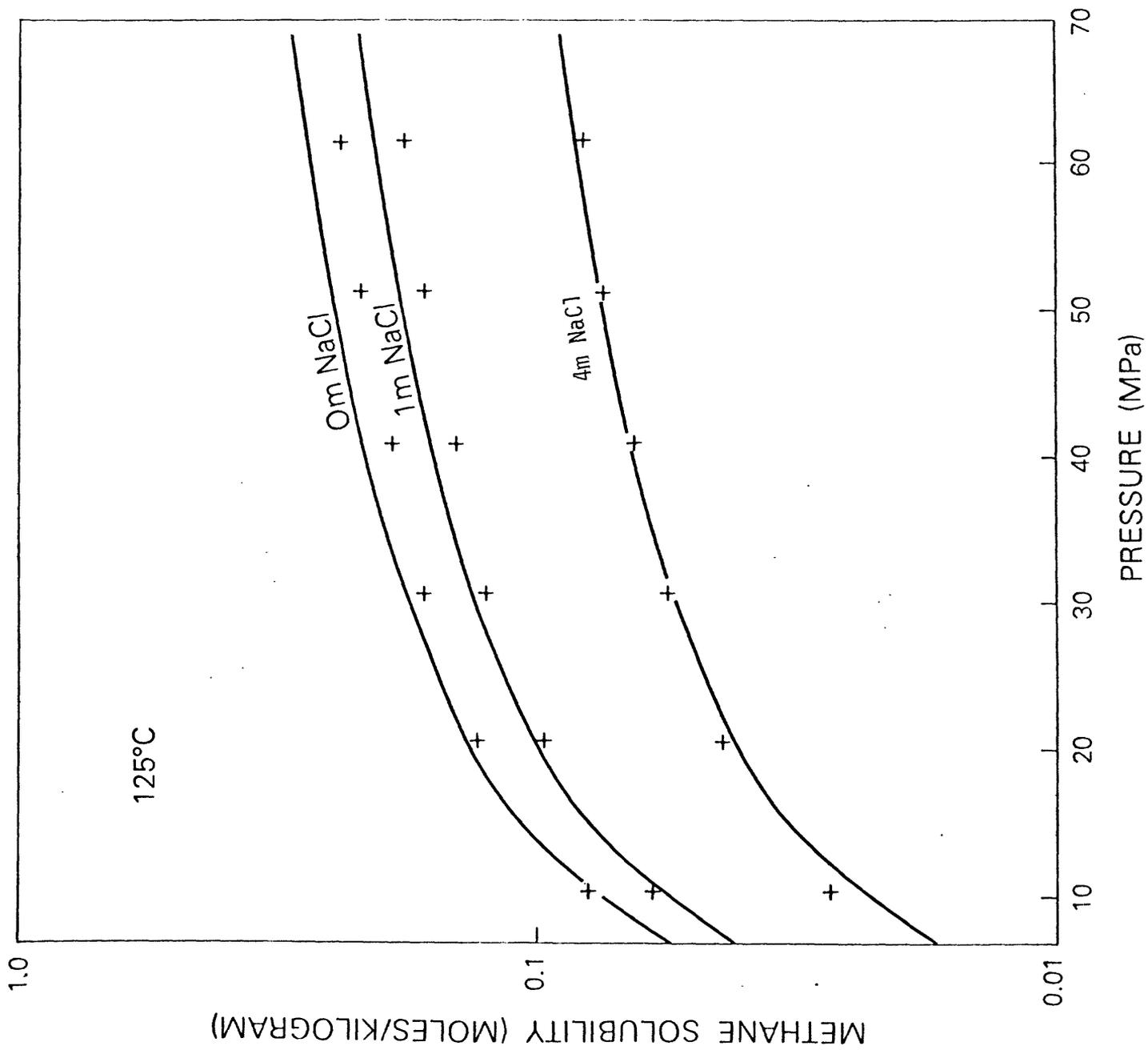


Figure 11.--Plot of $\log(S^{\circ}/S)$ versus weight % NaCl. The solid curve represents smoothed data from the present study. Salting-in would be represented by a curve falling below the zero line.

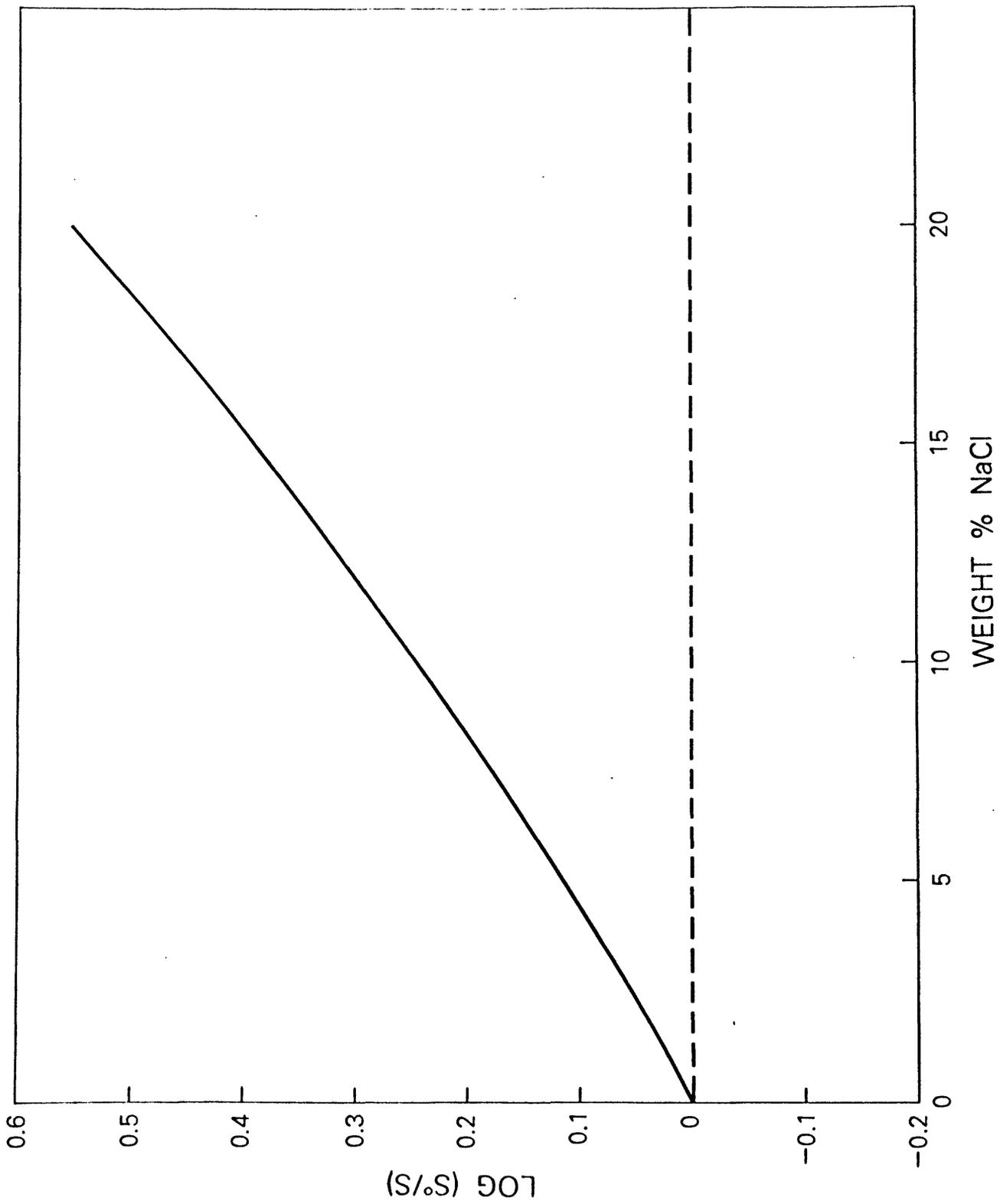


Figure 12.--Plot of % CH₄ (of the methane solubility in pure water) as a function of weight % NaCl. This plot can be used to estimate the solubility of methane in salt solutions from 0% to 20% NaCl, when only the solubility of methane in pure water at the same temperature and pressure is known. For example, in a solution of 10 weight % NaCl the solubility of methane is only 57% of that in pure water under the same temperature and pressure conditions.

