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The solubility of hydrocarbons in natural gas treating solvents represents lost product. In addition, hydrocarbons in the acid gas may potentially cause other problems in the processing of these waste streams. Thus, it is useful to be able to estimate the solubility of hydrocarbons in aqueous solutions of alkanolamines.

In this work, charts, built from a combination of a thermodynamic model and experimental data, are presented for the solubility of methane, ethane, and propane in water and in aqueous solutions of various industrially important alkanolamines. These charts should be useful to help design engineers make rapid estimations of the solubilities.

1.0 INTRODUCTION

Aqueous solutions of alkanolamines are commonly used to strip acid gas components (hydrogen sulfide and carbon dioxide) from natural gas and liquid hydrocarbons (such as liquefied petroleum gas [LPG]). One of the advantages of using aqueous solutions is that the solubility of hydrocarbons is low and thus the amount of valuable product lost is kept to a minimum.

Although usually quite small, in a detailed design the solubility cannot be assumed to be zero. Any hydrocarbon absorbed by the amine solution represents lost product, which ultimately ends up with the waste acid gas. Furthermore, the presence of the hydrocarbon in the acid gas may cause problems elsewhere in the process. For example, hydrocarbons may cause fouling of the catalyst in the Claus reactors.

In this work, the solubility of methane, ethane, and propane in water and in aqueous solutions of several industrially important amines are presented. A model is given to calculate the solubility. Using this model, charts of the solubilities were developed. These charts are useful for rapid approximation of the solubilities.

The model is based on experimental data available in the literature. Table 1 summarizes the experimental solubility measurements (some of these data were recently obtained and are only in the process of being published).

For the mixtures with just water, this table is not meant to be an exhaustive review, but these are the data upon which the model is largely based. Other data are available and were considered in the development of the model as well. On the other hand, the data listed for the amine solutions is believed to be the only data currently available in the literature.

2.0 THE MODEL

Typically the solubility of gases in liquids is modeled using a Henry's law approach. This work is no different. Carroll (1991) presents a discussion of the application of Henry's law to high pressure solubility. In the terminology of the paper of Carroll (1991), the model used in this work is the Krichevsky-Henry's law.

Properties of the non-aqueous phases were calculated using the Peng-Robinson (1976) equation of state.

The model used is detailed in Carroll and Mather (1997). The model can be applied to both gaseous and liquid hydrocarbons, as well as three-phase equilibrium.

2.1 Henry's Constants

The Henry's constants for the first three alkanes in water are shown in Fig. 1. These Henry's constants show a characteristic maximum. The maximum for methane is at 194°F, for ethane it is at 211°F, and finally for propane it is 218°F.

These maxima in the Henry's constants manifest themselves in minimum in the solubility. The temperature at which the isobaric solubility minima occur do not correspond exactly to the maxima in the Henry's constant, as will be shown later. These differences are a result of two effects: (1) the effect of temperature on the vapor pressure of the solvent (in this case water) and (2) deviations from ideality.

2.2 Salting-In Effect

The salting-out effect is a well-known phenomenon. Typically the solubility of a gas in an aqueous solution of an ionic salt is less than in pure water. However, for alkanolamines, the effect is opposite. The solubility of the light hydrocarbons is increased by the presence of the amine in the water; at least over the range of concentration of interest to the process engineer.

Basically, the model calculates the solubility of a given hydrocarbon in pure water, in terms of the mole fraction, and then corrects it for the presence of the alkanolamine. This is done using a salting-in ratio, S , where:

$$S_{ia} = \frac{x_{ia}}{x_{iw}}$$

where x_{iw} is the solubility of hydrocarbon i in water, expressed in mole fraction, and x_{ia} is the solubility of the hydrocarbon in the amine solution, also in mole fraction. These salting-in ratios are functions of several variables including the temperature and the amine concentration.

It has been found that the concentration effect can be adequately modeled using Setchenow coefficients, k . The two coefficients are related via the following equation:

$$\ln S_{ia} = k_{ia} C_a$$

where C_a is the amine concentration and it must be expressed as molarity (mol amine/L soln).

The Setchenow coefficients are a function of the temperature and the hydrocarbon-amine pair. Over the range of temperature studied in the lab, they are an increasing function of the temperature for all pairs studied to date.

The Setchenow coefficients are not a function of the pressure. In addition, they are not a function of the phase in which the hydrocarbon exists. That is, the same Setchenow coefficient can be used for gas or liquid hydrocarbons.

3.0 SOLUBILITY IN WATER

Figs. 2 through 4 show the solubility of methane, ethane, and propane in water. Although they appear to be significantly different, they share many common characteristics.

At first glance, it appears as though methane is more soluble than ethane and is significantly more soluble than propane. However, at low pressure the solubilities are very similar. For example, at 100°F and 100 psi, the solubilities are: methane: 2.3 SCF/100 gal, ethane: 3.7 SCF/100 gal, and propane: 2.1 SCF/100 gal.

3.1 Methane

The solubility of methane as predicted by the model is shown in Fig. 2. The prominent feature of this graph is the minima in the solubility at high pressure. This minima is well-known (see Culberson and McKetta, 1951) and was discussed earlier.

Note, also as discussed earlier, the minima are a weak function of the pressure. In addition, the minimal region is quite flat. In fact, over the range of temperature and pressure shown in Fig. 2, the solubility is quite insensitive to the temperature.

For methane, increasing the pressure has a significant effect on the solubility. This is partially due to methane remaining gaseous throughout this range of pressure and tempera-

ture. This explains the relatively high solubility of methane compared to either ethane or propane.

3.2 Ethane

The solubility of ethane in water is shown in Fig. 3. This has a similar appearance to that for methane except for a small three-phase (liquid-liquid-vapor) locus at low temperature. For pressures greater than the three-phase locus the solubility is for liquid ethane in water. For pressure below, the solubility is for gaseous ethane.

For temperatures slightly greater than the three-phase, although ethane is not a true liquid (it is a supercritical fluid), it exhibits similar properties. Thus, the solubility in this region is not as strong a function of pressure as one might expect (as it is for methane for example).

The high pressure curves for ethane in water show minima similar to those for methane.

3.3 Propane

Fig. 4 shows the solubility of propane in water. At first, this appears to be significantly different from the curves for either methane or ethane. However, it does share a few common characteristics.

For propane in water, the three-phase locus extends over a significant portion of the diagram. In fact, much of the figure is for the solubility of liquid propane in water. For pressures less than the three-phase locus the curves represent the solubility of gaseous propane in water. For pressure greater than the three-phase, the solubility is for liquid propane.

The curves for the solubility of gaseous propane tend to show an increase in the solubility with a decrease in temperature. However, the 500 psi isobar shows the opposite effect. All of these curves intersect the three-phase locus and have a cusp.

It can be seen from this plot that the solubility of liquid propane is fairly insensitive to the pressure. The curves for the solubility of liquid propane lie close together.

As with the other hydrocarbons, the solubility of propane in water exhibits minima. Unlike the other two hydrocarbons, this minimum is in the solubility of liquid propane and not the gas. This is a rather subtle difference.

4.0 THE SOLUBILITY IN AMINE SOLUTIONS

Results are presented graphically for several hydrocarbon in solutions various of alkanol-amine. These charts can be used for rapid approximation of the solubility and can thus be used to estimate the loss of hydrocarbons in the stripping process.

The solvents examined in this study, and some of their properties are listed in Table 2. Many of these values were calculated using the computer program described by Carroll (1994). The concentration of the solvents were taken as typical values that would be found in industrial application.

4.1 Methane in MEA, DEA, MDEA, DGA

There are more data available for the solubility of methane in alkanolamine solutions than there are for the other hydrocarbons. The solubilities in MEA, DEA, MDEA, and DGA were calculated using the model described earlier. These results are presented graphically in Figs. 5 through 8.

When expressed in terms of SCF/100 gal there appears to be only a relatively small effect of the presence of the amine on the solubility. This is partially because the conversion from mole fraction to the given units requires the density and molar mass of the amine solution. Both of these are larger for the amine solution than they are for water.

Table 3 lists the solubility for four temperatures and pressures. This table allows one to quickly determine the effect of amine concentration on the solubility; at least at these conditions. At 100°F, the solubility in the amine solution is only slightly larger than in water, except for MDEA where it is about 40% larger. On the other hand, at 200°F, the solubility increases significantly. In MEA and DEA, it is about 30% larger, whereas in MDEA and DGA, it is approximately double.

The plots for the solubility of methane in MEA, DEA, and MDEA look very similar to those for pure water. They show the solubility increasing with pressure and exhibit the characteristic minima. However, the presence of the amine changes the location of the minima.

The plot for the solubility of methane in DGA is significantly different from the others. In the 50 wt% solution there are still minima, but they are located at low temperature and are almost insignificant. Furthermore, at low pressure, below about 500 psi, the solubility is almost independent of the temperature. Data for the solubility of methane in water have been obtained for several amine concentrations and by two labs (see Table 1). This behavior was observed in the experimental data and is not a figment of the correlation.

4.2 Ethane in MDEA

Data for the solubility of ethane in amine solution are less common than those for methane. Jou et al. (1997a) report the solubility in 3 M MDEA and those data were incorporated into the model described earlier and extrapolated to 50 wt% (about 5.0 M), which is a more commonly used concentration in the gas processing industry. Since this represents a significant extrapolation, they should be considered less reliable than some of the other results in this paper.

Fig. 9 shows the calculated solubility of ethane in the 50 wt% solution. The figure is very similar to that for ethane in pure water presented earlier. This includes a small three-phase locus at low temperatures. The regions of liquid and vapor are as discussed earlier for ethane in water.

Even when expressed in the units of SCF/100 gal, the solubility is significantly larger in the amine solution than in water. For example, at 100°F and 500 psi the solubility in pure water is about 10 SCF/100 gal, whereas in the amine it is about 21 SCF/100 gal.

4.3 Propane in MDEA

A very thorough experimental investigation of the phase equilibria in the system 3 M MDEA + propane was performed by Carroll et al (1992). This involved measuring the vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibria. Compositions of all components in all phase were measured. It was from this detailed investigation that subsequent approximations were made (such as the amount of amine in the non-aqueous phases is negligibly small).

As with the values for methane and ethane, the propane data were extrapolated to 50 wt% MDEA using the thermodynamic model outlined earlier. Since these represent a significant extrapolation, they should be considered less reliable than some of the other results in this paper.

Again, this plot is similar to that for the solubility of propane in water. Over much of the range of temperature shown on this plot, there is a three-phase locus. In addition, the solubility of liquid propane in the MDEA is quite insensitive to the pressure. However, the solubility of the liquid propane in the amine does not show the minima that it does in pure water. This is similar to the behavior observed for methane in DGA and thus is not entirely without precedent.

The solubility of propane in the amine is significantly larger than in pure water. For example, at 100°F and 100 psi (at these conditions, the propane is a gas) the solubility in pure water is about 2.1 SCF/100 gal, whereas in the amine it is about 5 SCF/100 gal. Furthermore, the solubility of liquid propane in water at 100°F is about 3.7 SCF/100 gal, where as in the amine it is about 9 SCF/100 gal.

5.0 DISCUSSION

Presented in this work are charts for the solubility of three light hydrocarbons in water and in aqueous solutions of alkanolamines. These charts demonstrate the effect of pressure, temperature and the presence of the amine on the solubility. They should be useful tools for the rapid estimation of the solubility.

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7.0 NOMENCLATURE

7.1 Symbols

C	concentration, molarity
k	Setchenow coefficient
S	salting-in coefficient
x	mole fraction

7.2 Subscripts

i	hydrocarbon (methane, ethane, or propane)
ia	hydrocarbon-amine pair
iw	hydrocarbon-water pair

7.3 Abbreviations

DGA	diglycolamine
DEA	diethanolamine
M	molarity (moles of amine per liter of solution)
MDEA	methyldithanolamine
MEA	monoethanolamine
SCF	standard cubic feet
TEA	triethanolamine

TABLE 1 A Summary of Experimental Investigations into the Solubility of Hydrocarbons in Water and Aqueous Solutions of Alkanolamines

Solute	Solvent	Concentration	Reference
methane	water	—	Culberson and McKetta (1951)
methane	water	—	Crovetto et al. (1982)
methane	MEA	15 and 40 wt%	Lawson and Garst (1976)
methane	MEA	3.0 M	Carroll et al. (1997)
methane	DEA	5, 25, and 40 wt%	Lawson and Garst (1976)
methane	DEA	3.0 M	Carroll et al. (1997)
methane	DGA	50 wt%	Dingman (1976)
methane	DGA	3.0 and 6.0 M	Jou et al. (1997a)
methane	TEA	3.0 M	Carroll et al. (1997)
methane	MDEA	3.0 M	Jou et al. (1997b)
ethane	water	—	Culberson and McKetta (1950)
ethane	MEA	15 and 40 wt%	Lawson and Garst (1976)
ethane	DEA	5 and 25 wt%	Lawson and Garst (1976)
ethane	TEA	2.0, 3.0, and 5.0 M	Jou et al. (1996)
ethane	MDEA	3.0 M	Jou et al. (1997b)
propane	water	—	Kobayashi and Katz (1953)
propane	MDEA	3.0 M	Carroll et al. (1992)

TABLE 2 Properties of Solvents Examined in This Study

		Water	MEA	DEA	MDEA	DGA
Concentration:	Weight %	—	15	30	50	50
	Mole %	—	4.95	6.85	13.15	14.64
	Molarity	—	2.48	2.96	4.39	5.01
Density:	kg/m ³	1000	1006	1037	1045	1052
	lb/ft ³	62.4	62.8	64.7	65.2	65.7
	lb/gal	8.31	8.40	8.65	8.72	8.78
Molar Mass:	g/mol	18.015	20.147	23.980	31.317	30.770

TABLE 3 A Few Points for the Solubility of Methane in Water and Amine Solutions (in SCF/100 gal)

	100°F 100 psi	100°F 1000 psi	200°F 100 psi	200°F 1000 psi
water	2.3	19	1.6	15
MEA (15 wt%)	2.6	22	2.0	19
DEA (35 wt%)	2.5	21	2.0	20
MDEA (50 wt%)	3.3	27	3.0	29
DGA (50 wt%)	2.8	23	3.0	29

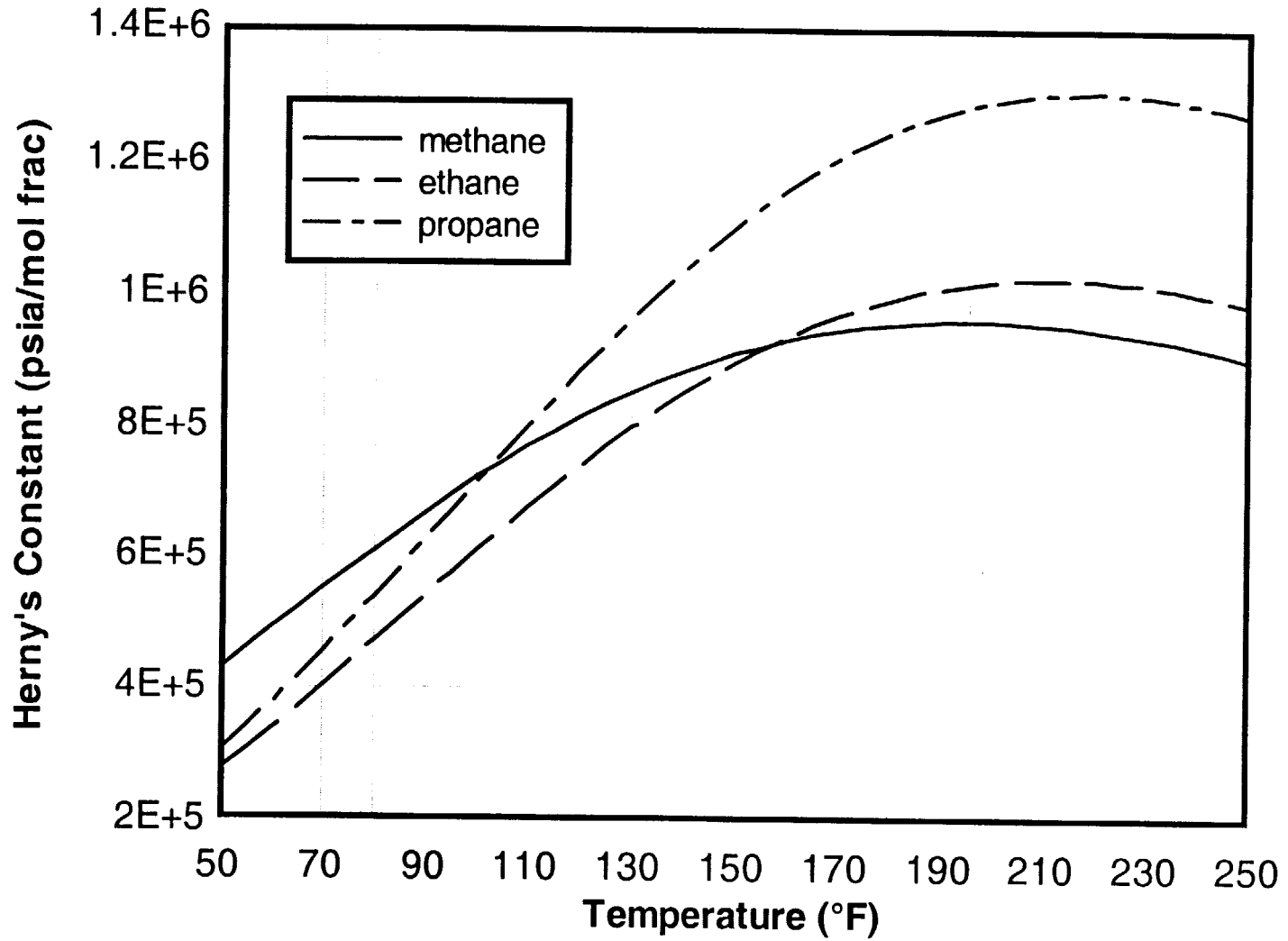


Fig. 1 The Henry's Constants for Methane, Ethane, and Propane in Water

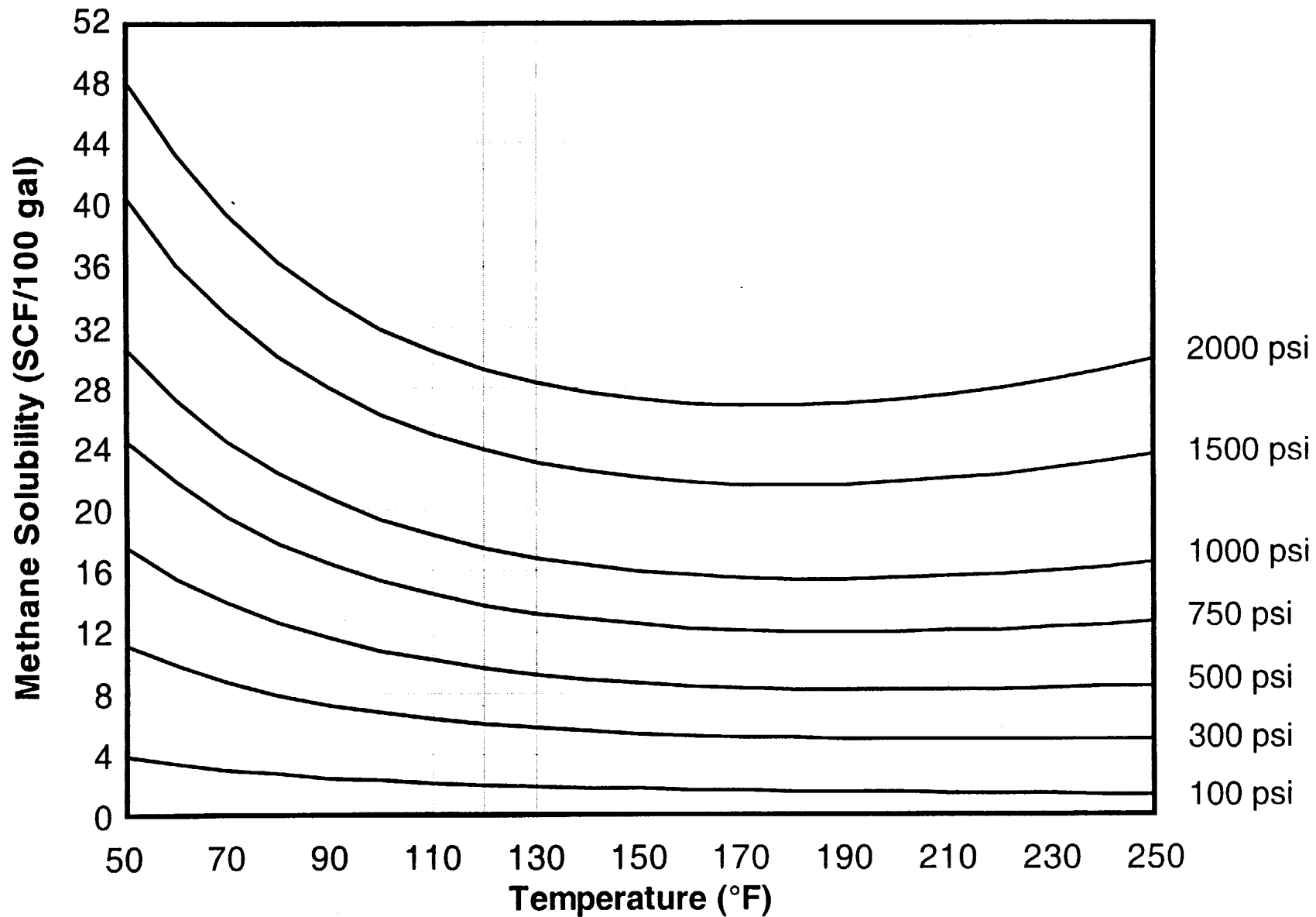


Fig. 2 The Solubility of Methane in Water

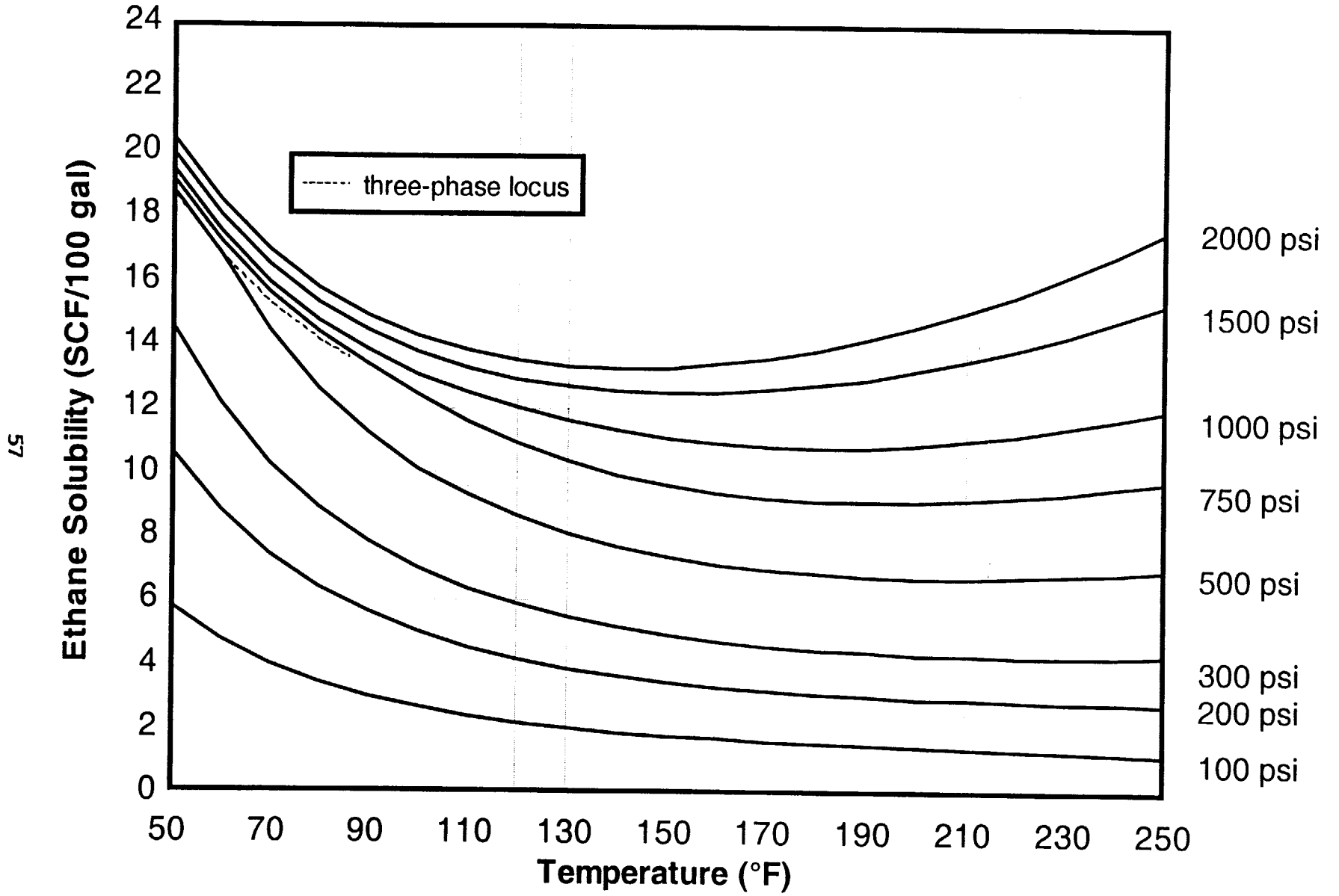


Fig. 3 The Solubility of Ethane in Water

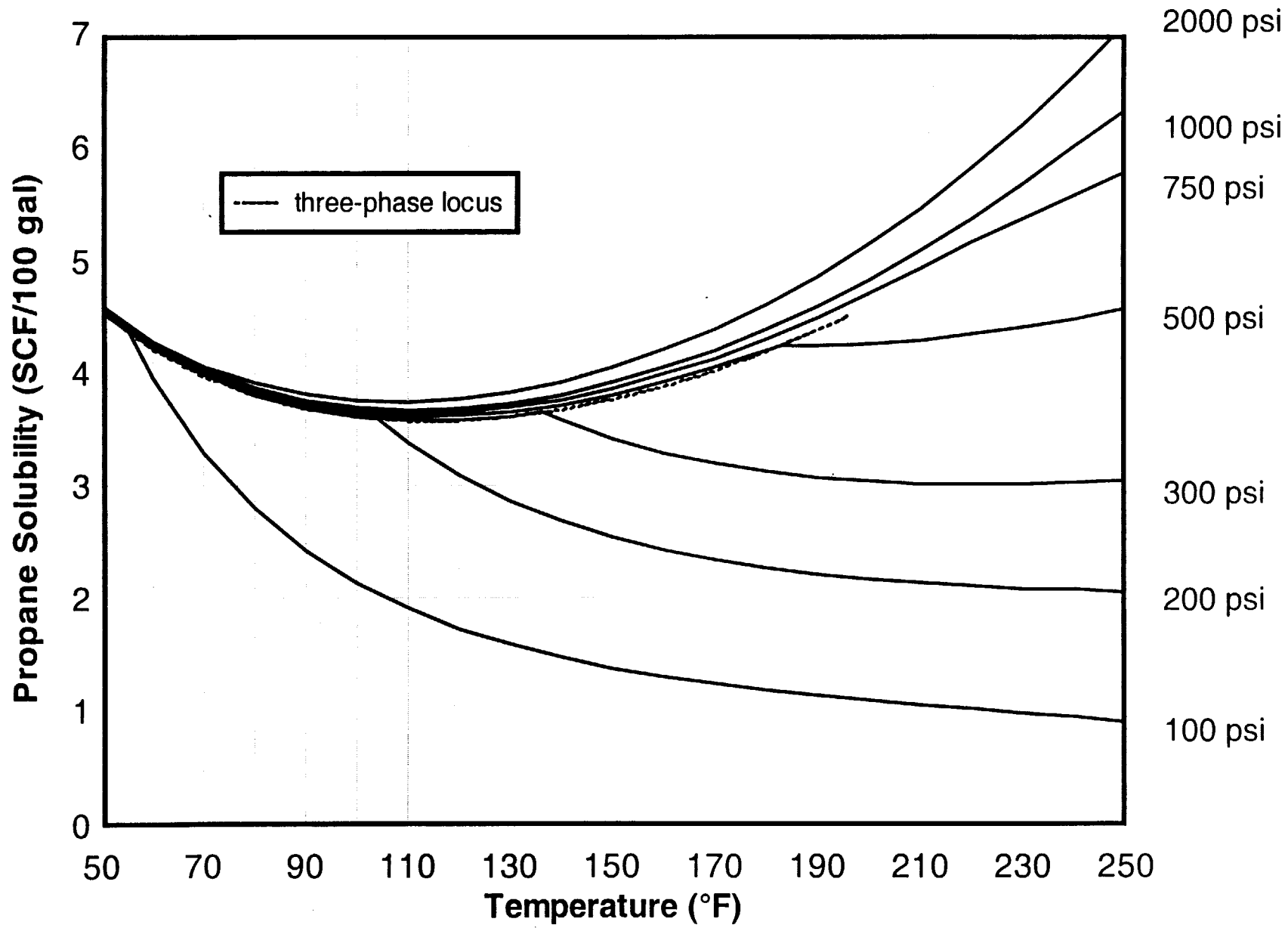


Fig. 4 The Solubility of Propane in Water

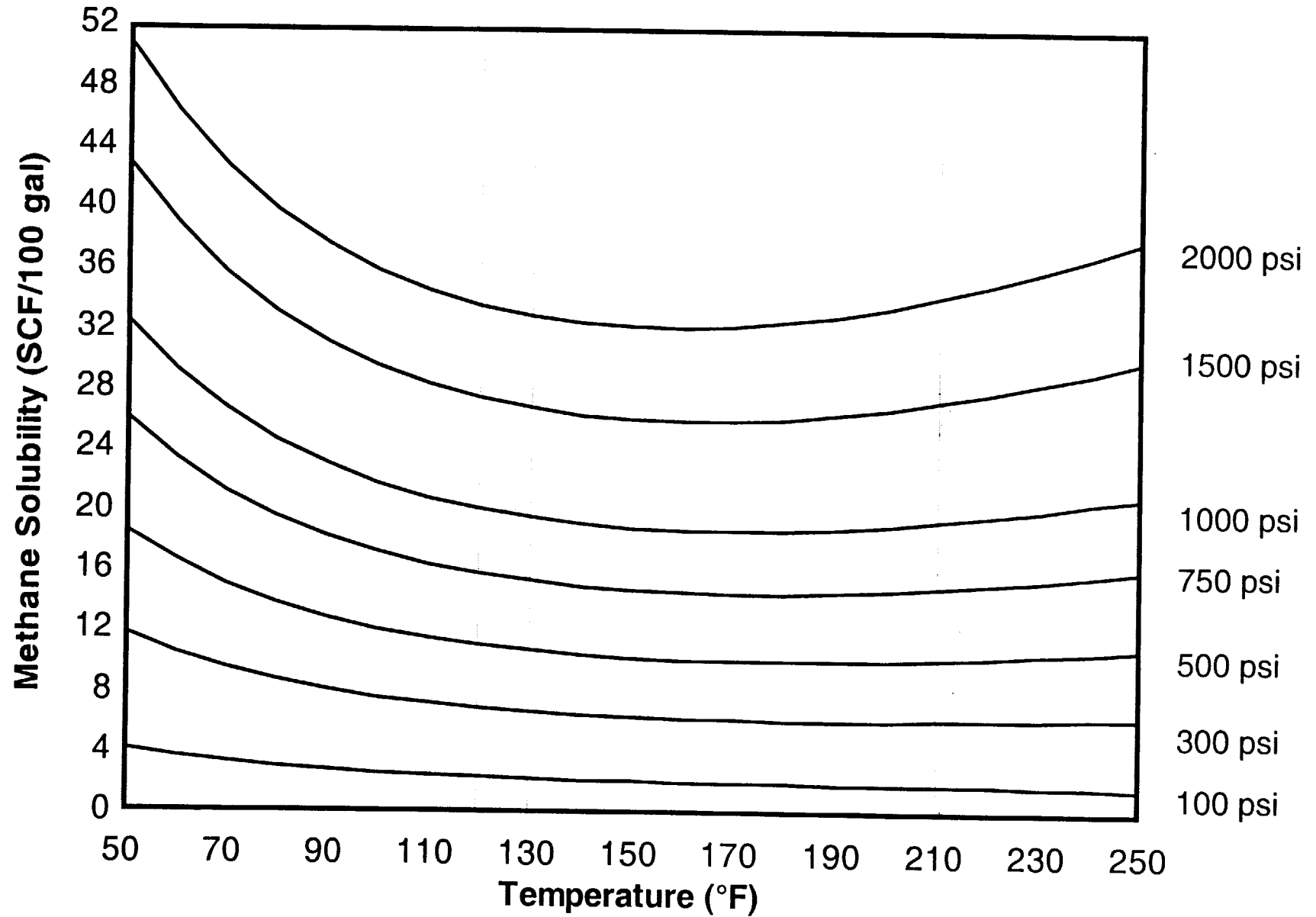


Fig. 5 The Solubility of Methane in a 15 wt% MEA Solution

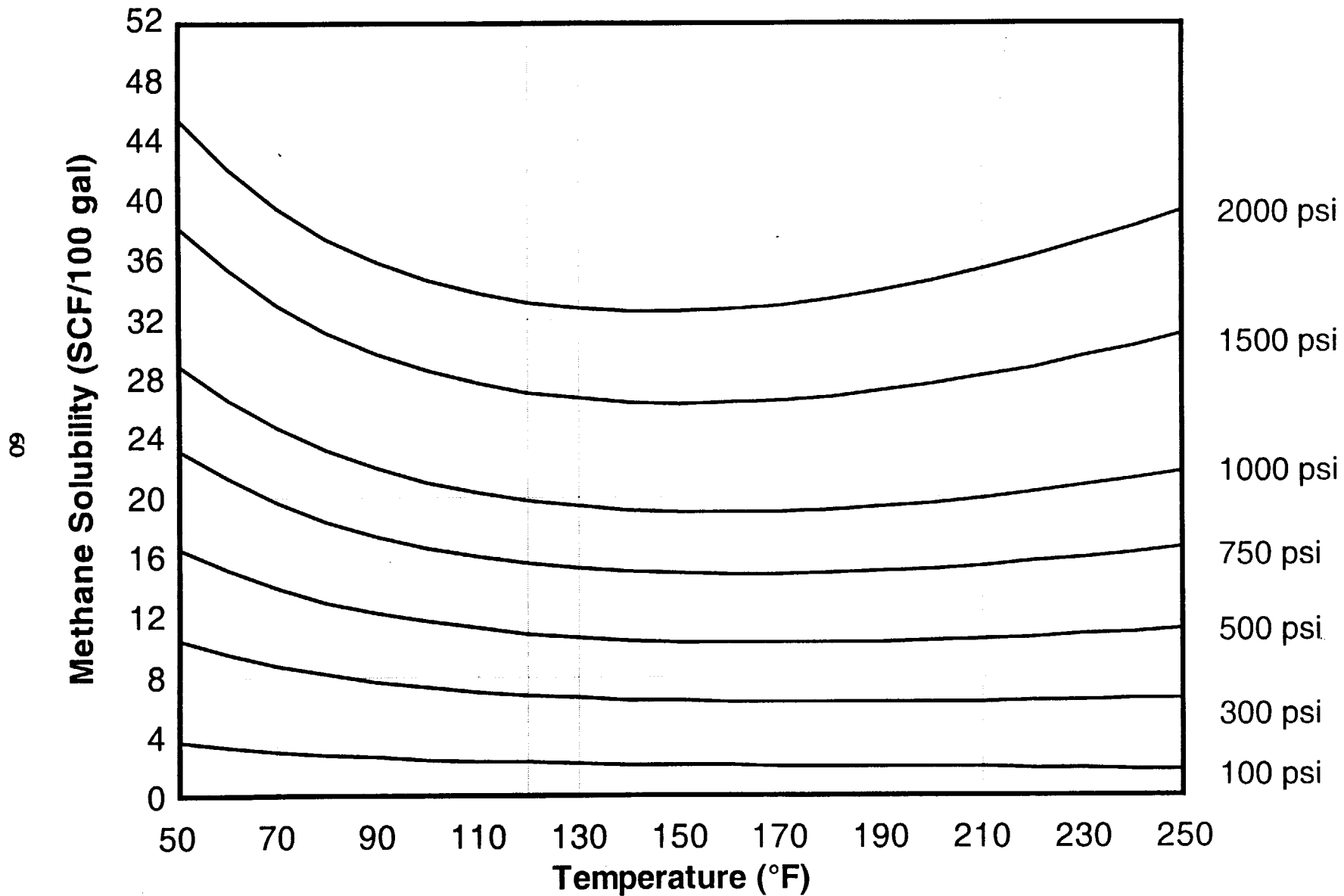


Fig. 6 The Solubility of Methane in a 35 wt% DEA Solution

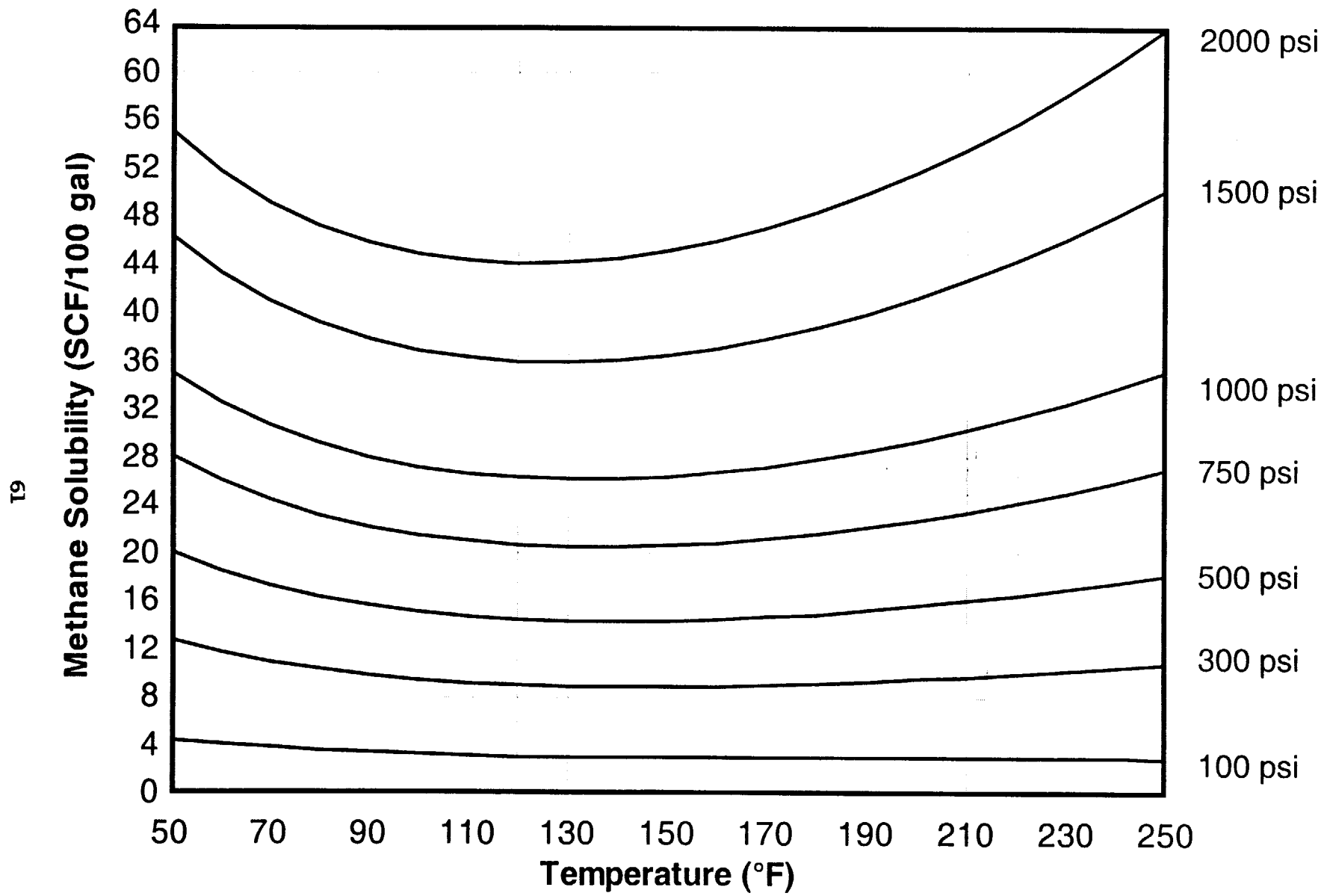


Fig. 7 The Solubility of Methane in a 50 wt% Solution of MDEA

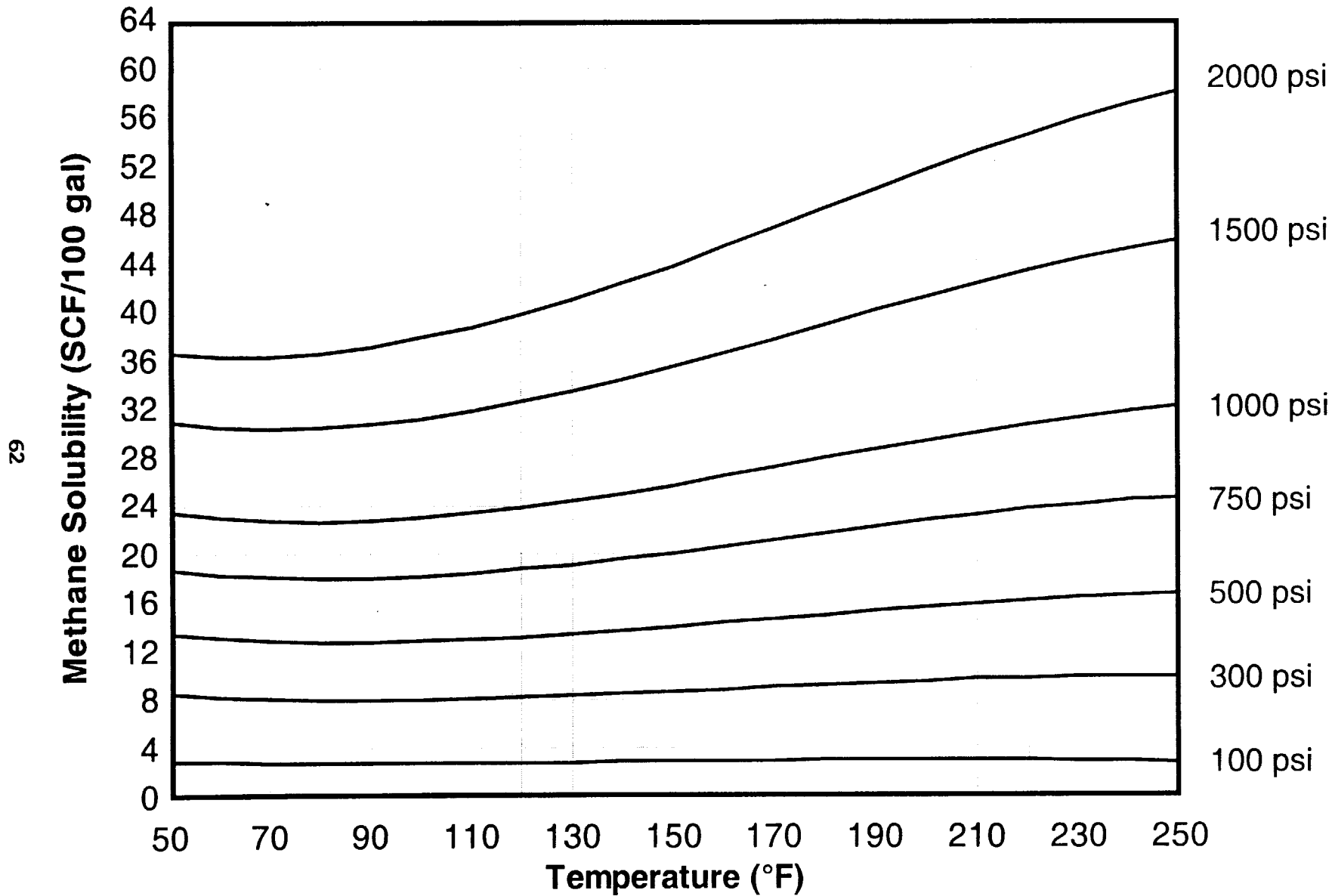


Fig. 8 The Solubility of Methane in a 50 wt% Solution of DGA

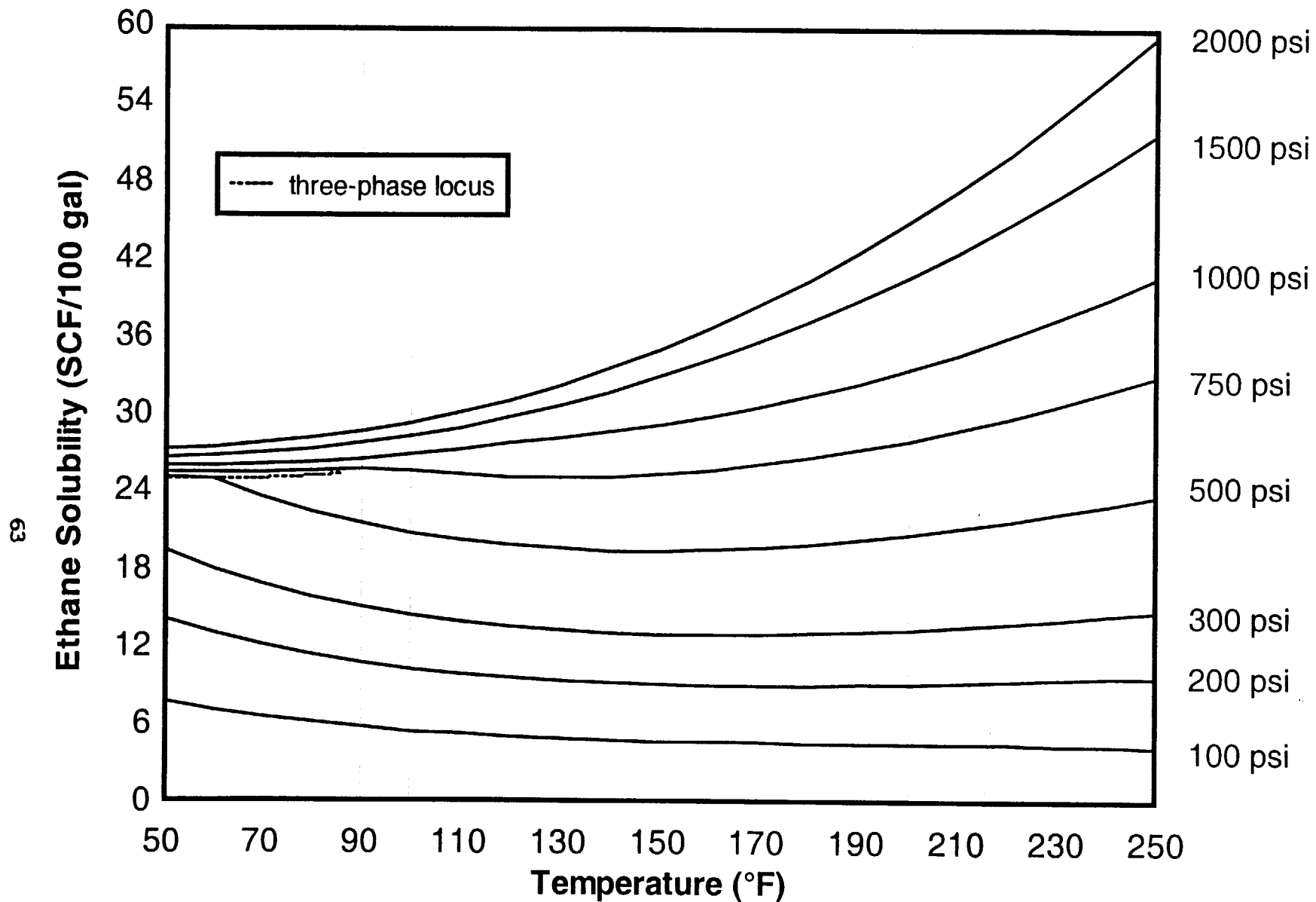


Fig. 9 The Solubility of Ethane in a 50 wt% Solution of MDEA

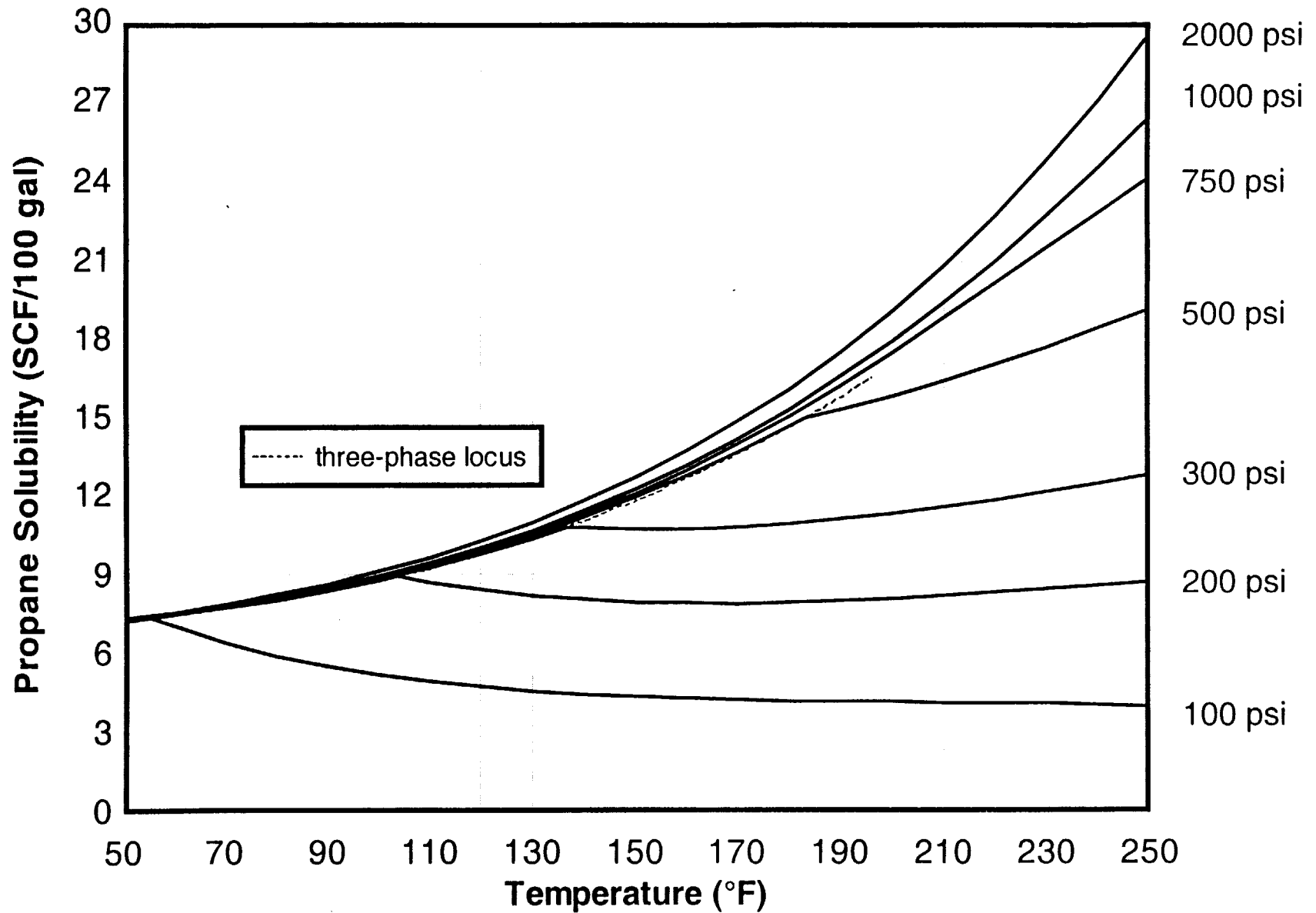


Fig. 10 The Solubility of Propane in a 50 wt% Solution of MDEA