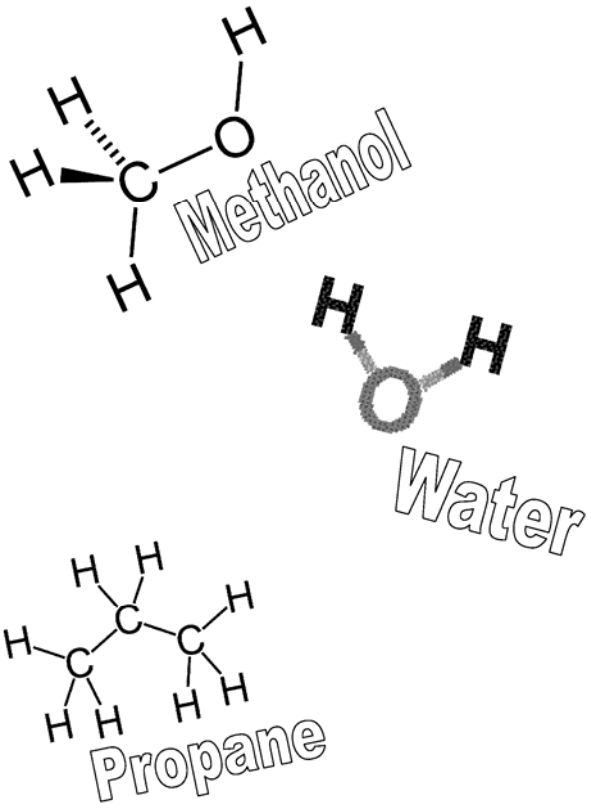


REPORT

Use of Methanol for Controlling Water Freezing in LP Gas

Docket 11992

PROPANE
EXCEPTIONAL ENERGY®

To

Propane Education

& Research Council

1140 Connecticut Ave. NW, Suite 1075

Washington, DC 20036

Battelle
The Business of Innovation

May 2007

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Docket 11992

Final Report

to

Propane Education & Research Council
1140 Connecticut Ave. NW, Suite 1075
Washington, DC 20036

May 2007

by

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Use of Methanol for Controlling Water Freezing in LP Gas – Final Report

Executive Summary

Maintaining and expanding the market for LP gas* requires continual attention to product quality in order to prevent operational problems and maintain customer satisfaction. One fuel quality issue that can arise is the presence of water in the fuel. A small amount of water can dissolve in liquid propane. The amount of water that can be dissolved varies with the temperature: as the temperature goes down, the solubility of water in propane decreases substantially. Thus, if the liquid propane cools through expansion or due to low ambient temperatures, liquid water may come out of solution, leading to the formation of a separate water layer in a tank. And if propane vapor contains too much water vapor, cooling upon pressure reduction can lead to ice formation in valves and regulators, a situation that can cause operational problems for the fuel user.

The ideal remedy for water freezing issues would be to ensure that the water content of the fuel was so low that such problems could not occur. However, for a variety of reasons, water contamination occasionally happens.

It has long been known that the addition of methanol to propane can reduce or eliminate fuel freezing problems: the methanol acts as an antifreeze and prevents whatever water that may be present from freezing. Many propane suppliers find that even high moisture content propane can be acceptable to end users without freeze-up complaints if enough methanol has been added.

However, the use of methanol has the potential to cause operational problems with some newer appliances that are sensitive to fuel composition. And, when LP gas is used as a fuel for internal combustion engines, the presence of excessive methanol has the potential to cause problems with engine calibration or with increased emissions. Moreover, if there is enough water and methanol, a separate water-methanol layer may form at the bottom of fuel storage tanks. This mixture is more corrosive than LP gas fuel.

For these reasons the addition of excessive amounts of methanol is to be avoided. Guidelines are needed, therefore, that will allow LP gas producers, distributors, and large users to ascertain the amount of methanol that is actually needed. In order to develop such guidelines, it is necessary to know about the physical behavior of LP gas, methanol and water.

This document discusses the physical behavior of LP gas, methanol, and water, and methods of measuring the concentrations of water and methanol, as well as possible implications for fuel tank corrosion and fuel vaporization.

* The terms “LP gas fuel” and “propane” are generally used interchangeably in the United States and in this report.

Understanding of the Technical Basis for Methanol Use

Even though the physical chemistry data for systems containing propane, water, and methanol are not complete, considerable insight into the behavior of methanol as an antifreeze can be obtained. This insight has been used to make some recommendations for methanol use. However, additional data are needed on the solubility of methanol in propane and on the degree to which this solubility changes with temperature and with water content. More data are also needed to define the K ratios that describe how the amount of methanol in propane vapor is related to the amount methanol in the liquid propane.

The development and validation of an equation of state[*] for the propane-water-methanol system would provide a theoretical foundation for describing the complete behavior of this system. Although past equations of state could not handle such highly non-ideal situations, recent (post year 2000) advances indicate that developing a reasonably accurate equation of state for propane-water-methanol would now be feasible.

Implications for the Behavior of Propane Fuel Systems

It is useful to examine the implications of the phase[†] and solubility behavior on the behavior of propane fuel systems in the presence of water and methanol.

- **Dry Fuel Systems** – If the LP gas fuel is completely dry, then, clearly, both the liquid propane and the vaporized gas will be water free. But because the solubility limit for water in propane has not been reached, if any water or moisture is present, the liquid propane has the ability to absorb some or all of it.
- **Fuel Systems with Some Dissolved Water** – If the liquid propane that is delivered to the distributor has some dissolved water, there are several possibilities. If the amount of water is small, less than 20 ppm, the water will remain in solution in the liquid, even as the propane cools to winter storage temperatures.

  However, if the amount of water is greater than 20 ppm, the water can come out of solution as the propane cools. Initially, this water will form small droplets, but, because the density of liquid water is greater than that of liquid propane, this water will eventually form a water layer on the bottom of the tank.

Once a water layer has formed, the diffusion of water into liquid propane is so slow that even if the propane warms or is replaced by drier fuel, the water will not readily go back into solution, but will remain as a lingering source of moisture.

[*] "Equation of state" is a thermodynamic equation describing the state of matter under a given set of physical conditions. It provides a mathematical relationship between two or more properties such temperature, pressure, volume, or internal energy.

[†] "Phase" refers to a state of matter that is uniform throughout, not only in chemical composition, but also in physical state. "State" refers to being a solid, liquid, or gas.

If there is water in the liquid propane, there will also be water in the propane vapor. In fact, because of the K ratio, there will be a 4 to 10 times greater concentration of water in the vapor than in the liquid.

If this vapor is cooled, liquid water will condense, and the amounts of condensed water can be considerable. It may be readily appreciated that if even a portion of this water condenses and freezes in a valve or regulator, blockages can occur quickly.

Measurement of Water and Methanol

None of the existing methods for measuring water and methanol are sufficiently accurate, free from interferences and usable in the field. Currently, portable and relatively-inexpensive meters based on the absorption of infrared light are used by field technicians monitor ppm levels of other gases, such as carbon dioxide.

Advances in optical and electronic technologies have made feasible the development of an instrument that would allow the measurement of ppm-levels of both water and methanol in the field. Based on experience with carbon dioxide meters for HVAC applications, it is believed that such a meter would ultimately cost about $500. If usable monitoring meters for water and methanol can be made available, much of the uncertainty associated with limiting water content and managing methanol addition would be removed.

Clearly the biggest knowledge gap is the lack of an accurate, practical, and reliable field method for measuring the amount of water and methanol in fuel.

The NDIR method shows promise and the development of the NDIR technique for the determination of the methanol content of propane is recommended. Algorithms need to be developed that relate the amount of water and methanol to the optical absorption at key wavelengths. It is also recommended that measurements be made to better quantify the relative concentrations of methanol in the propane liquid and propane vapor (K-ratio).

In addition, because length-of-stain tubes offer convenience at low cost, they will undoubtedly continue to be used and therefore more should be done to quantify the effects of methanol on the reading for water vapor, as well as to qualify their accuracy with LP gas fuel and their susceptibility to interference from methanol.

Much work might be done with the valve-freeze test to better control the test conditions in the hope of reducing the variability of the test and to account for the possible presence of methanol. However, considering the magnitude of the effort required and the likelihood that the valve-freeze test will never provide more than a crude indication of water content, resources are better directed towards the NDIR test that has the potential to provide both water and methanol content quickly and accurately.

Effect of Methanol on Materials

There are some data gaps and uncertainties concerning the action of propane with added methanol on aluminum cylinders, on some elastomers and with regards to stress cracking. However, overall, neither the technical literature nor the long experience with methanol indicates that there are significant materials problems.

Effect of Methanol on Fuel Vaporization

No significant problems are indicated. The main uncertainty is that data are lacking to clearly define the limiting amounts of water and methanol in propane, and the limiting temperature conditions, beyond which a separate water- or methanol-rich layer will be formed. If liquid from such a layer were vaporized and/or fed to combustion equipment, there would be operational problems.

Alternatives to Methanol

A systematic examination of all chemical compounds with appropriate properties did not identify any alternatives that would be superior to methanol. Moreover, no candidates were identified that would be able to match methanol's combination of effectiveness, relative lack of operational problems, and low cost.

Usage Recommendations

By making some reasonable assumptions about the amount of water that could be dissolved in liquid propane, the relationship of the water and methanol composition of vapor derived from that liquid, and the amount of methanol needed to protect the water in that vapor from freezing, it is possible to estimate the amount of methanol needed. This is about 450 mass ppm of methanol in the liquid propane. Applying a safety factor to account for uncertainty in our knowledge of the physical chemistry, a methanol addition rate of 600 mass ppm is recommended.

This addition rate is equivalent to 4.9 volume ounces of methanol per 100 gallons of propane, or 49 volume ounces (slightly more than 3 pints) per 1000 gallons.

Action Recommendations

The following are considered key action recommendations:

- Develop an optical water and methanol meter for field use.
    - *Significance: Knowing the water and methanol concentration will make a significant difference in the ability to prevent fuel quality issues.*
- Obtain K-ratio data for methanol in propane.
    - *Significance: Current values are only estimates even though these data are necessary to guide the amount of methanol used as an antifreeze.*
- Obtain data on the effect of water on methanol solubility in appropriate concentration range.
    - *Significance: There are continued issues with the formation of water layers.*
- Quantify the effects of methanol on the stain-tube readings for water vapor.
    - *Significance: Length-of-stain tubes will continue to be used, so we should know more about their behavior.*
- Develop an accurate equation of state for propane-methanol-water.
    - *Significance: The equation of state can become the theoretical basis for future studies.*

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Abbreviations

atm – atmosphere (unit of pressure)

kPa – kilopascals; 1,000 pascals (unit of pressure)

MMscf – million standard cubic feet, a common measure for volume of gas. Standard conditions are normally set at 60 F and 14.7 psia
MPa – megapascals; 1,000,000 pascals (unit of pressure)

NDIR – **N**on-**D**ispersive **I**nf**r**ared (type of detector)

ppm – parts per million (unit of concentration)

psi – pounds per square inch (unit of pressure); may be absolute (psia) or gage (psig, relative to atmospheric pressure)

Wobbe Index – an indicator of the interchangeability of fuel gases; calculated by *higher heating value/(square root of gas specific gravity*

Introduction

Background

Maintaining and expanding the market for LP gas fuel[*] requires continual attention to product quality in order to prevent operational problems and maintain customer satisfaction.

One fuel quality issue that can arise is the presence of water in the fuel. Even though water has a low solubility in propane [at 20 C (68 F), the solubility of water in propane is only about 180 mass ppm[†]], the water can come out of solution as the propane cools through expansion or due to low ambient temperatures. This process may lead to the formation of a water layer in a tank. And if propane vapor contains too much water vapor, cooling upon pressure reduction can lead to ice formation in valves and regulators, a situation that can cause operational problems for the fuel user.

The ideal remedy for water freezing issues would be to ensure that the water content of the fuel was so low that such problems could occur. However, for a variety of reasons, water contamination occasionally happens.

It has long been known that the addition of methanol to LP gas fuel can reduce or eliminate fuel freezing problems: the methanol acts as an antifreeze and prevents whatever water that may be present from freezing. Many propane suppliers find that even wet fuel can work without freeze-up complaints if enough methanol has been added.

However, although the use of methanol may not affect the burners used by most residential, commercial, industrial, or agricultural customers, excessive amounts have the potential to cause operational problems with some newer appliances that are more sensitive to fuel composition. And, when LP gas is used as a fuel for internal combustion engines, the use of excessive methanol has the potential to cause problems with engine calibration, resulting in increased emissions. Moreover, if there is enough water and methanol in the propane, a separate water-methanol layer may form at the bottom of fuel storage tanks. This methanol-water mixture can be more corrosive than LP gas fuel.

For these reasons the addition of excessive amounts of methanol is to be avoided.

Guidelines are needed, therefore, that will allow LP gas manufacturers, distributors, and large users to ascertain the amount of methanol that is actually needed. In order to develop such guidelines, it is necessary to know about the physical behavior of LP gas, methanol and water.

This document discusses the physical behavior of LP gas, methanol, and water, and methods of measuring the concentrations of water and methanol, as well as possible implications for fuel tank corrosion and fuel vaporization.

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[*] The terms “LP gas fuel” and “propane” are generally used interchangeably in the United States and in this report.

[†] For liquid and solid solutions is customary to use mass ppm, defined as the mass of solute divided by the mass of solvent times 10^6. For gases, it is customary that the term ppm refers to the volume fraction times 10^6.

Because commercial LP gas in the U.S. consists primarily of propane, and because freezing is primarily an issue with propane, the technical analysis presented in this report will focus primarily on propane. (The vapor pressure of butane is low enough that the amount of cooling resulting from the expansion of butane in valves and regulators is seldom enough to cause ice formation. Also, because of this low vapor pressure (0 psig at 31 F), butane is typically not used in cold climates and therefore ice formation is unlikely.]

Contents

This document is organized in sections as follows:

- Summary of what is known about the physical and chemical properties of the propane-methanol-water system
- Discussion of methods for the measurement of water and methanol concentrations in LP gas fuel
- Materials impacts
- Impacts of methanol addition on LP gas fuel vaporization
- Guidelines for the use of methanol as an antifreeze
- Examination of possible alternatives to methanol for antifreeze use
- Principal conclusions
- Bibliography of relevant literature
- Literature references cited in this report

Physical Chemistry of LP Gas, Water and Methanol

The discussion of the physical chemistry of the LP gas-water-methanol system begins with a brief review of the physical properties of each of these substances and then focuses on solubility. This information sets the stage for the subsequent discussion of how these propane, water, and methanol substances interact with each other as liquids and on the composition of the resulting vapors.

Physical Properties of LP Gas, Water, and Methanol

This brief description of the some of the properties of LP gas, water and methanol is intended to provide a framework for the discussion of LP gas fuel freezing issues.

Properties of LP Gas

LP gas is composed of a mixture of hydrocarbons, principally, propane and butane, with small amounts of ethane and propane and smaller amounts of heavier hydrocarbons. In the U.S. LP gas is usually nearly all propane with only small amounts of butane or other hydrocarbons. Thus, in discussing the properties of LP gas fuel it is common to consider mainly the properties of propane.

Basic property data for propane and butane are shown in Table 1. Figure 1 shows the vapor pressures of propane and butane, as a function of temperature.[*] For the purpose of subsequent discussions on fuel freezing issues, we highlight the following characteristics:

- Propane is a gas under ambient temperatures and pressures, but can be stored as a liquid. The vapor pressure of propane is about 900 kPa at 20 C (130 psig at 70 F). Butane is a significantly less volatile liquid with a vapor pressure of about 100 kPa at 20 C (17 psig at 70 F).
- The critical temperature and pressure of propane are 96.7 C and 4.25 MPa (206 F and 616 psig). Thus, at common environmental temperatures of -20 to 40 C (-4 F to 104 F), the reduced pressure[†] of propane ranges from 0.06 to 0.32. These reduced pressures justify the approximation that the propane and butane vapors be considered ideal gases at the environmental temperatures commonly encountered.[‡]
- When liquid propane evaporates or propane vapor is reduced in pressure, cooling occurs.

[*] Because LP gas fuel is generally more than 90 percent propane, the vapor pressure curve for LP gas fuel is close to that shown for propane.

[†] The reduced pressure is defined as the actual pressure divided by the pressure at the critical point, which is where gas density has increased to the point that gas and liquid can no longer be distinguished. Gases whose reduced pressure is relatively low tend to behave as "idea" gases. Reduced pressure is unitless.

[‡] As the reduced pressure become closer to 1, the gas is closer to the critical point and therefore difficult to represent with an "ideal" gas model.

Table 1. Properties of LP Gas Fuel, Water, and Methanol

Property	Propane	Butane	Water	Methanol
Formula	C_3H_8	C_4H_{10}	H_2O	CH_3OH
Molecular weight	44.097	58.124	18.02	32.04
Dipole moment, D	0.084[1]		1.85[1]	1.70[1]
Density, liquid at 20 C (68 F), kg/m^3	500[2]	579[2]	998[1]	791.4[3]
Vapor pressure @ 20 C, kPa	850[2]	210[2]	2.34[1]	12.8[3]
@ 68 F, psi	123	30	0.34	1.9
Boiling pt, degrees C	-42.1[2]	-0.5[2]	100[1]	64.6[3]
degrees F	-44	31	212	148
Critical temperature, degrees K	370[2]	425[2]	647[1]	512[3]
degrees C	97[2]	152[2]	374[1]	239[3]
Critical pressure, MPa	4.266[2]	3.796[2]	22.064[1]	8.084[3]
Critical compressibility factor	0.225[2]	0.228[2]	0.235[4]	0.224[3]
Heat of vaporization at 25 C, kJ/kg	425[5]	386[5]	2260[1]	1168[3]

[1] Handbook of Chemistry and Physics.
[2] Matheson Gas Data Book.
[3] "Technical Information & Safe Handling Guide for Methanol."
[4] Properties of Gases and Liquids.
[5] Internal Combustion Engines and Air Pollution.

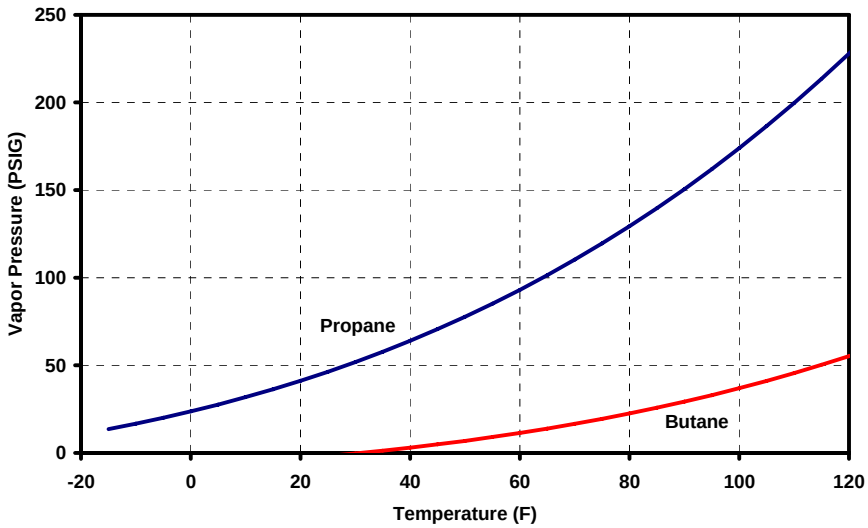


Figure 1. Vapor Pressures of Propane and Butane

Propane is generally stored as a liquid, but used as a gas and must therefore vaporize prior to use. Because of the heat required for vaporization, substantial cooling can occur as the propane evaporates, resulting in very low temperatures. The amount of evaporative cooling may be calculated from the heat of vaporization and specific heat.

For example, consider propane stored as a liquid at 32 F that expands to a vapor at 1.5 psig or 40 inches of water. In the absence of any heat transfer from the surroundings to the propane, evaporation of the liquid would lower the temperature to about -112 F.

Propane is generally used at a pressure that is much less than the pressure in the storage tank. Therefore, regulators are installed that reduce the supply pressure to a low (inches of water) value through a throttling process. This process results in cooling of the gas; the amount of cooling for a given reduction in pressure is given by the Joule-Thomson coefficient. Figure 2 shows values for the Joule-Thomson coefficient for propane as a function of temperature and pressure (from Thermodynamic Properties of Propane). Figure 3 shows a similar graph in English units (from Phase Equilibria in Hydrocarbon Systems). It may be seen that for common temperature and pressures this coefficient is about 0.2 to 0.3 degrees F/psi. Thus, a reduction of pressure of 690 kPa (100 psi) results in a cooling of the propane vapor of about 15 C (25 F). If the propane vapor contains water, such a temperature decrease can lead to blockages from ice in valves and regulators.

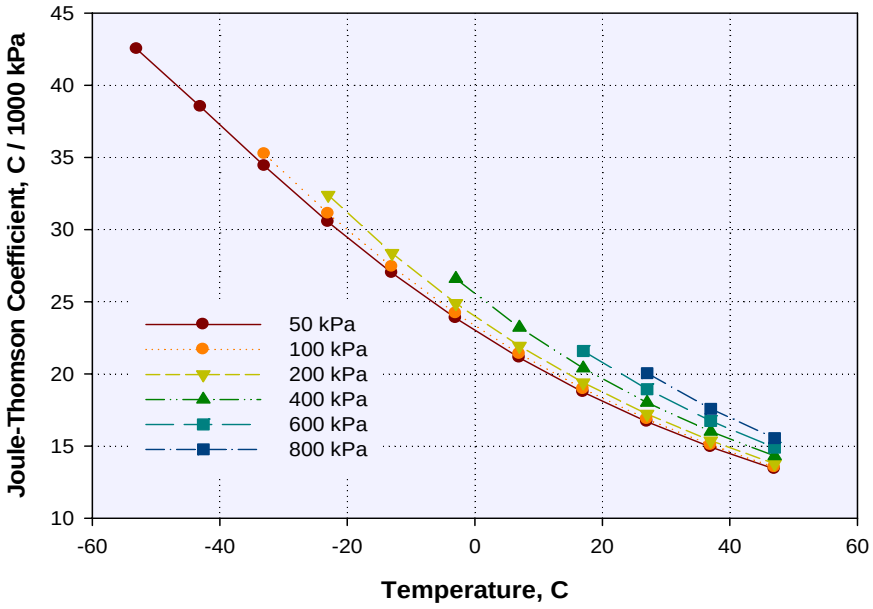


Figure 2. Joule-Thomson Coefficients for Propane

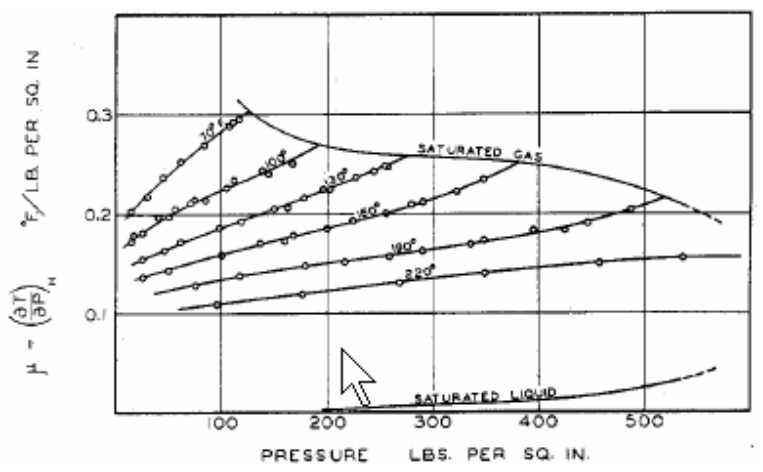


Figure 3. Joule-Thomson Coefficient for Propane, English Units

Properties of Water and Methanol

Water is a familiar substance and its properties are well known. Some properties of water relevant to this discussion are summarized in Table 1. Vapor pressure data for water are shown in Figure 4.

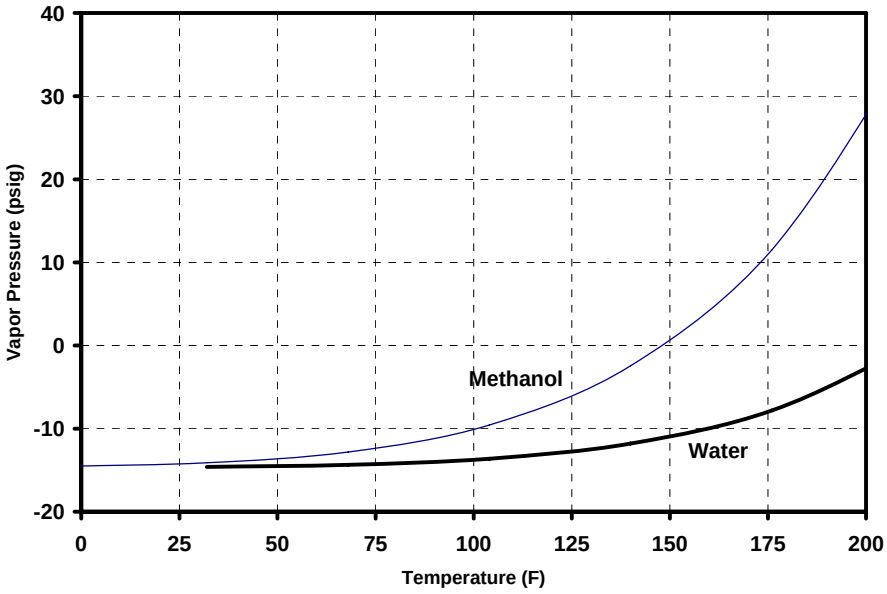


Figure 4. Vapor Pressure of Methanol and Water

Liquid water is remarkably non-volatile considering that water molecules are small, with a molecular weight of only 18. This is because the water molecules, being polar, interact with each other to form hydrogen bonds. However, as will be discussed later, when small amounts of water are dissolved in liquid propane, the interaction between water molecules and propane

molecules is much weaker than the interaction among water molecules, and so the effective vapor pressure of water in propane is much higher. This is reflected in the observation that when propane contains dissolved water, the fraction of water in propane vapor is greater than would be expected from fraction of water in the liquid propane or from the vapor pressure of water alone at that temperature.

Relevant properties of methanol are also summarized in Table 1. The variation in vapor pressure of pure methanol with temperature is shown in Figure 4. However, like water, although the vapor pressure of pure methanol is greatly reduced by the interactions among methanol molecules, so that when methanol is dissolved in propane the interactions between methanol molecules and propane molecules are weaker and the vapor pressure is higher than would be expected.

Solubility and Phase* Behavior of Propane-Water, Propane-Methanol and Propane-Water-Methanol Systems

The previous section on physical properties has summarized some basic data on the properties of propane, water, and methanol. Now we consider the solubility and phase behavior of propane, water, and methanol. First, we present some background information related to solubility (Phase and Solubility Background). The next section (Phase and Solubility Behavior of Propane-Water and Butane-Water Systems) examines properties of the binary propane-water and butane-water systems; the following section (Phase and Solubility Behavior of the Propane-Methanol System) examines properties of the binary propane-methanol and butane-methanol systems. The final section (General Relationship Between Liquid and Vapor Compositions) provides a summary of what is known about propane-water-methanol ternary system.

Phase and Solubility Background

Meaning of Phase

Liquid propane is a phase and propane vapor is also a phase. A phase may consist of two or more chemical components. For example, a mixture of liquid methanol dissolved in liquid propane is a phase. Depending on the temperature and pressure, the same substance or mixture of substances can exist in different phases.

Properties Which Affect Solubility

Liquids whose molecules have similar properties, particularly those with a similar electrical charge distribution, tend to dissolve in one another.† Chemically, the distribution of electric

* "Phase" refers to a state of matter that is uniform throughout, not only in chemical composition, but also in physical state. "State" refers to being a solid, liquid, or gas.
† Sometimes stated as the "Like dissolves like" rule.

charge is measured by the dipole moment[*], and molecules are often divided into "polar" and "non-polar" based on their dipole moments. Propane and water differ greatly in the magnitude of their electrical dipole moments: the dipole moment for water is quite high and that for propane is quite low. In other words, water is quite polar and propane is quite non-polar. Therefore, we expect the solubility of water in propane (and the solubility of propane in water) will be minimal, and in fact this is the case. We also expect that water and methanol, which are both quite polar, will be mutually soluble, and in fact they are miscible.[†]

Solubility is also affected by temperature. For gases dissolved in liquids, higher temperature generally leads to reduced solubility. For solids and liquids dissolved in liquids, higher temperature often results in greater solubility.

Solubility Units

In this report we generally use parts per million (ppm) by mass as the unit of solubility because we believe it is the most straightforward. This is simply the mass of solute[‡] divided by the mass of solution[§] multiplied by 10^6. The chemical literature often contains solubility data in terms of mole fraction or mole ppm. The mole fraction is the number of moles of solute divided by the number of moles of solution. The mole ppm is the mole fraction multiplied by 10^6.

The conversion from mass ppm to mole ppm and vice versa depends on the molecular weight of the substances involved. For water in propane, 100 mass ppm is equal to 245 mole ppm. For methanol in propane, 100 mass ppm is equal to 138 mole ppm.

Phase and Solubility Behavior of Propane-Water and Butane-Water Systems

Phase Behavior of Propane-Water System

The phase behavior of the propane-water system is described in detail by Harmens and Sloan (in "The Phase Behavior of the Propane-Water System"); their graphical description is shown in Figure 5. This diagram, which is not drawn to scale, is applicable for pressures from 562 to 4242 kPa (81 to 615 psia). [**] The diagram shows regions of temperature and composition where propane and water exist as a solid, liquid, or vapor phase, or as instances where two phases can exist together. Note that the phase behavior of the propane – water system is complicated by the formation of propane hydrate. In this context, the term "hydrate" refers to a solid combination of water and a hydrocarbon, such as propane. In a hydrate, the water molecules form a lattice that can contain propane or other hydrocarbon molecules. Propane hydrates can exist as solids at temperatures well above the normal melting point of either water or propane.

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[*] The dipole moment is a measure of the separation of the positive and negative charges in a molecule. If there is charge separation, one end of the molecule will be more negative than the other end. The direction and magnitude of this charge separation is referred to as the dipole moment.

[†] Miscible means that two liquids can be mixed in any proportion without phase separation, that is, without the formation of two distinct layers.

[‡] The solute is the substance that is dissolved.

[§] For concentrations in the ppm range, the mass of solution and the mass of solvent are essentially equal.

[**] Their paper also contains similar diagrams for other pressure ranges.

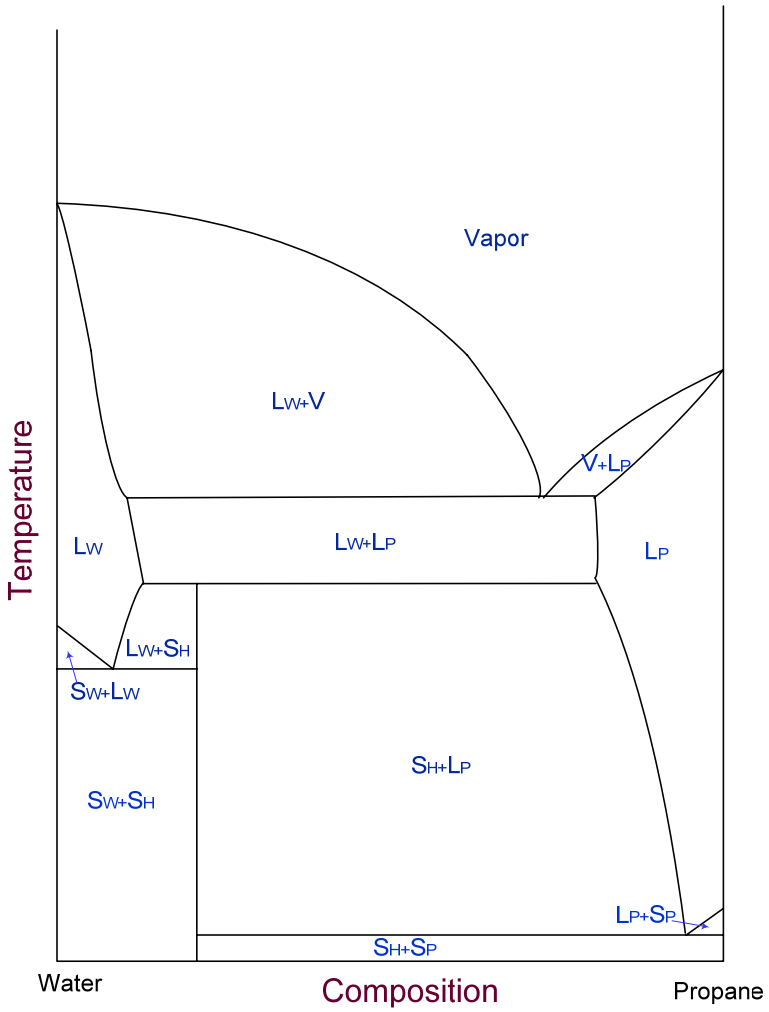


Figure 5. Temperature-Composition Diagram for Propane-Water System

On the diagram, phases are indicated as follows:

V = vapor	SW = solid water (ice)
LW = water-rich liquid	SP = solid propane
LP = propane-rich liquid	SH = solid propane hydrate

Solubility of Water in Propane and Butane

Water is soluble in propane and butane to only a slight extent. A graph of the solubility of water in propane and butane is shown in Figure 6. This graph is based on graphical data in the *Engineering Data Book*. Note that the solubility of water in propane decreases with temperature.

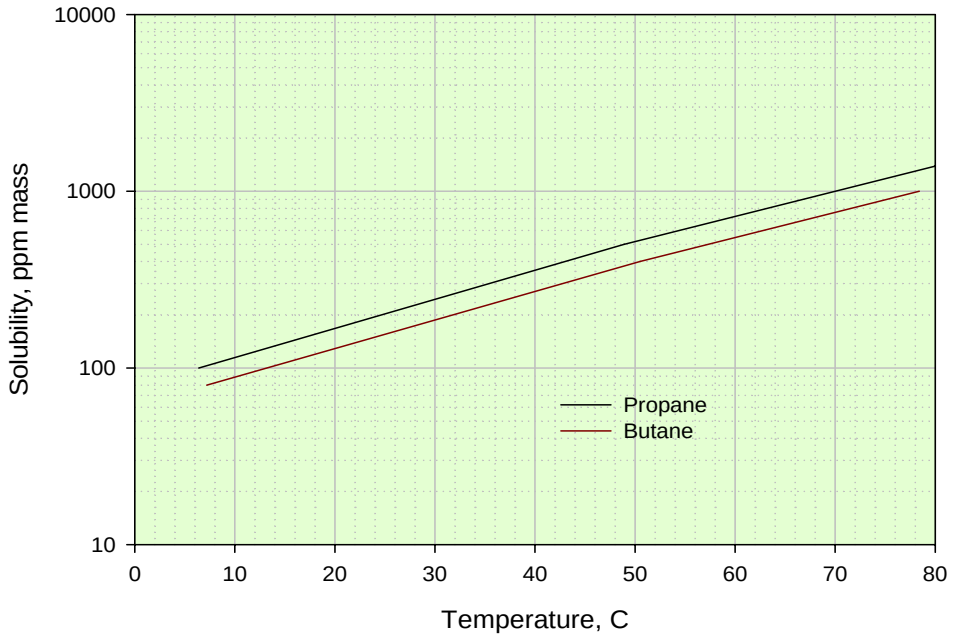


Figure 6. Solubility of Water in Propane and Butane

Tabular data for the solubility of water in liquid propane and n-butane are given in the book by Williams and Lom (*Liquefied Petroleum Gases).* These data are reproduced in Table 2.

Note that the solubility of water in propane decreases greatly at the temperature decreases. This means that the same unit of propane at 38 C (100 F) could contain more than four times the water as would be possible at 0 C (32 F).

Table 2. Solubility of Water in Propane and Butane at Various Temperatures

Hydrocarbon	Temperature, C	Temperature, F	Solubility, mass ppm
Propane	0	32	65
Propane	21	70	140
Propane	38	100	280
Propane	54	130	550
Propane	71	160	1,100
Propane	88	190	2,400
n-Butane	0	32	16
n-Butane	21	70	60
n-Butane	38	100	150
n-Butane	54	130	330
n-Butane	71	160	680
n-Butane	88	190	1,400

Solubility of Propane and Butane in Water

Hayduk and Battino (*Propane, Butane, and 2-MethylPropane*) reviewed 13 experimental studies of the solubility of propane in water. Their summary of these data are shown in Table 3. Note that the solubility of propane in water is considerably less than the solubility of water in propane. Battino (in *Propane, Butane, and 2-MethylPropane*) also reviewed 16 papers on the solubility of butane in water. The summary of these data are also shown in Table 3. Note that butane is substantially more soluble in water than propane.

Table 3. Solubility of Propane and Butane in Water

Temperature, C	Temperature, F	Propane Solubility in Water, ppm	Butane Solubility in Water, ppm
0	32	29.6	215
20	68	13.1	87
40	104	7.6	46

Phase and Solubility Behavior of the Propane-Methanol System

Phase Behavior of Propane-Methanol System

Some data and descriptions of the phase behavior of the propane-methanol system are available, but are mainly for relatively high temperatures.

Robinson, et al. ("Development of the Peng-Robinson Equation") show the phase behavior of methanol and propane at a range of temperatures from 38 C (100 F) to 204 C (400 F). Their data are reproduced in Figure 7. Note that in this temperature range, there is only one liquid phase: there is no formation of separate propane-rich and water-rich layers.

Figure 8 shows a pressure-composition diagram for the propane-methanol system at 40 C (104 F) based on data are from Joung, et al. (in "High-Pressure Vapor-Liquid Equilibrium Data"). Again, at this temperature there is only one liquid phase.

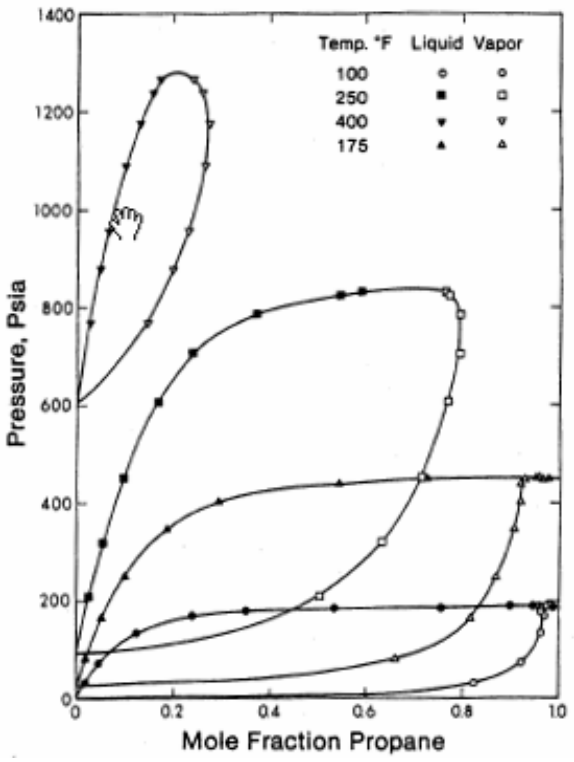


Figure 7. Phase Behavior of Propane-Methanol System at Various Temperatures

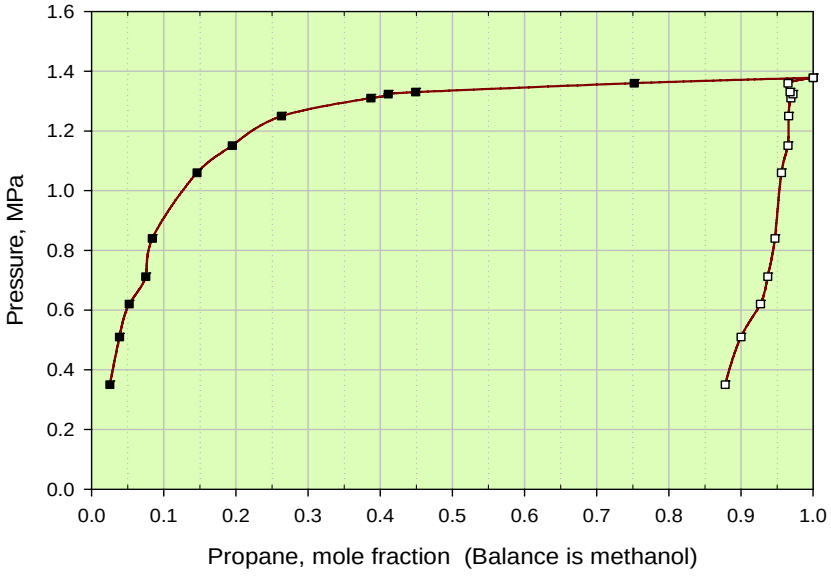


Figure 8. Vapor-Liquid Equilibrium Data for Propane-Methanol at 40 C (104 F)

Existence of an Azeotrope

One detail not indicated in the previous propane-methanol phase diagrams is the probable existence of a propane-methanol azeotrope. An azeotrope (or an azeotropic solution) is a liquid solution which evaporates or boils without changing composition because the composition of the liquid and the vapor are the same. A calculated model (in IVCSEP Newsletter) of the behavior of the methanol-propane system shows the existence of an azeotrope at a composition of 0.0067 mole fraction methanol in propane (equal to 6,700 mole ppm or 5,000 mass ppm). Figure 9 shows these results. The existence of the azeotrope is undoubtedly one reason for the effectiveness of methanol as an antifreeze – it cannot be separated from propane by evaporation (the process normally encountered in a propane storage tank as fuel is withdrawn in vapor form) and therefore "follows" the propane as it changes from liquid to vapor.

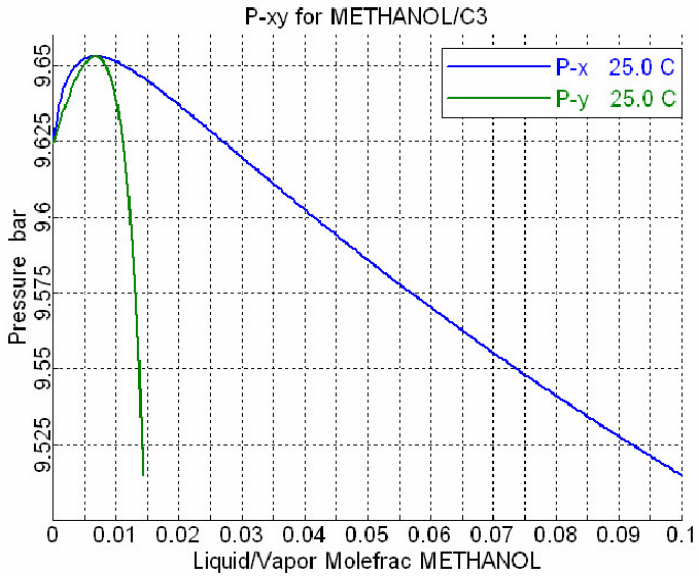


Figure 9. Calculated Methanol-Propane Behavior Showing Azeotrope

Solubility of Methanol in Propane and Butane

Figure 7 and Figure 8 show the behavior of the propane-methanol system at 40 C (104 F) where there is only one liquid phase. For many solutions, including propane and methanol, there is a critical solution temperature below which the liquid separates into two phases: a propane-rich phase with dissolved methanol and a methanol-rich phase with dissolved propane.

Below the critical solution temperature we may speak meaningfully of the methanol solubility in propane and butane. According to Francis (in *Critical Solution Temperatures*), the critical solution temperature for propane-methanol is about 21 C (70 F) and is weakly dependant on total pressure, ranging from 21 C at 10 atm (150 psig) to 19 C (66 F) at 46 atm (675 psig).

However, comparison with data for butane suggests that the critical solution temperature for propane-methanol may be lower. Noda, et al. (in Ternary Liquid-Liquid Equilibria) report a

critical solution temperature for the n-butane-methanol system of -7.4 C (19 F) and provide cloud point data for methanol in butane over a range of compositions. A plot of their cloud point data are shown in Figure 10. The cloud point is the point at which two phases begin to appear in solution, leading to a cloudy appearance. The cloudy appearance is due to very small droplets of non-miscible liquid. Thus, the cloud point data show clearly that at temperatures above -7.4 C, (corresponding to the peak of the cloud point curve in Figure 10 at a methanol mass fraction of about 0.26) all mixtures of n-butane and methanol are miscible.

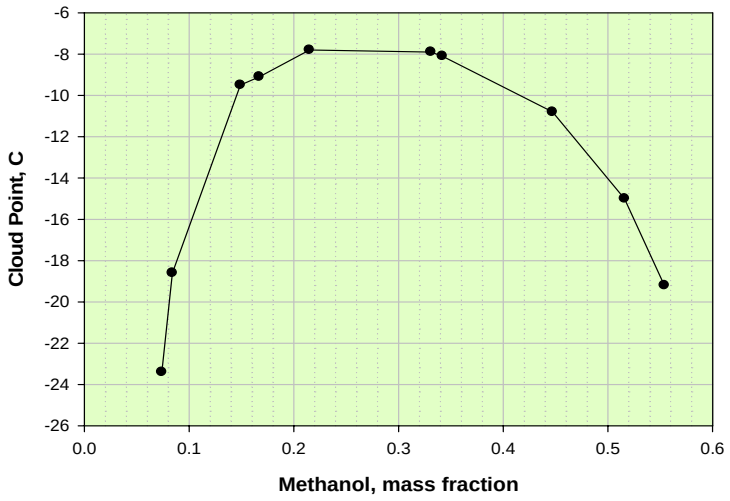


Figure 10. Cloud Point Data for n-Butane-Methanol System

Although Noda, et al. do not provide cloud point or critical solution temperature data for propane-methanol, based on the greater similarity of molecular size we expect that methanol will be more soluble in propane than in butane. It is not clear how this expectation can be reconciled with the critical solution temperature reported by Francis. We would also expect that methanol will be less soluble in pentane and other longer alkanes and in fact this prediction is confirmed by experimental data (Kiser, et al., "Critical solution temperatures in methanol").

In theory, data on the solubility of methanol in propane at 20 C and 0 C could be obtained by reading from the graphs in Figure 11 and Figure 12 at the scale location where the water concentration is zero. In practice, it is not possible to obtain a meaningful result.

Solubility of Propane and Butane in Methanol

Data on the solubility of propane in methanol are reviewed by Hayduk (in *Propane, Butane, and 2-MethylPropane*). Data for butane are found in Kretschmer and Wiebe (in Solubility of Gaseous Paraffins). These solubility data are shown in Table 4. Note that the solubility of propane and butane in methanol is about 1000 times the solubility in water.

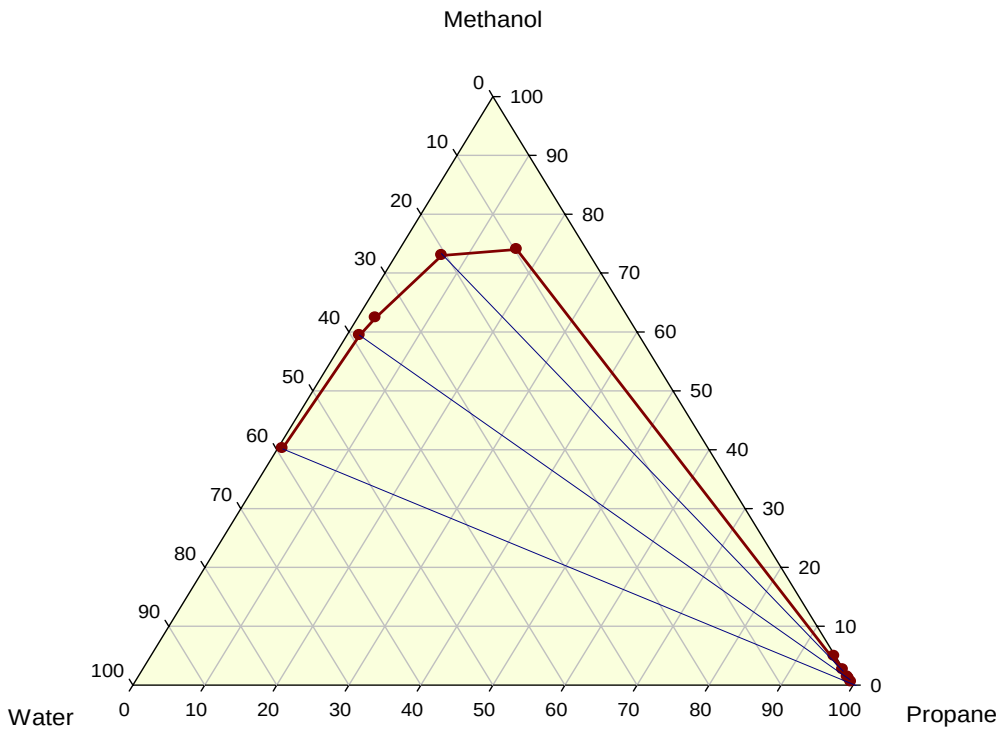


Figure 11. Phase Diagram for the Propane-Water-Methanol System at 20 C

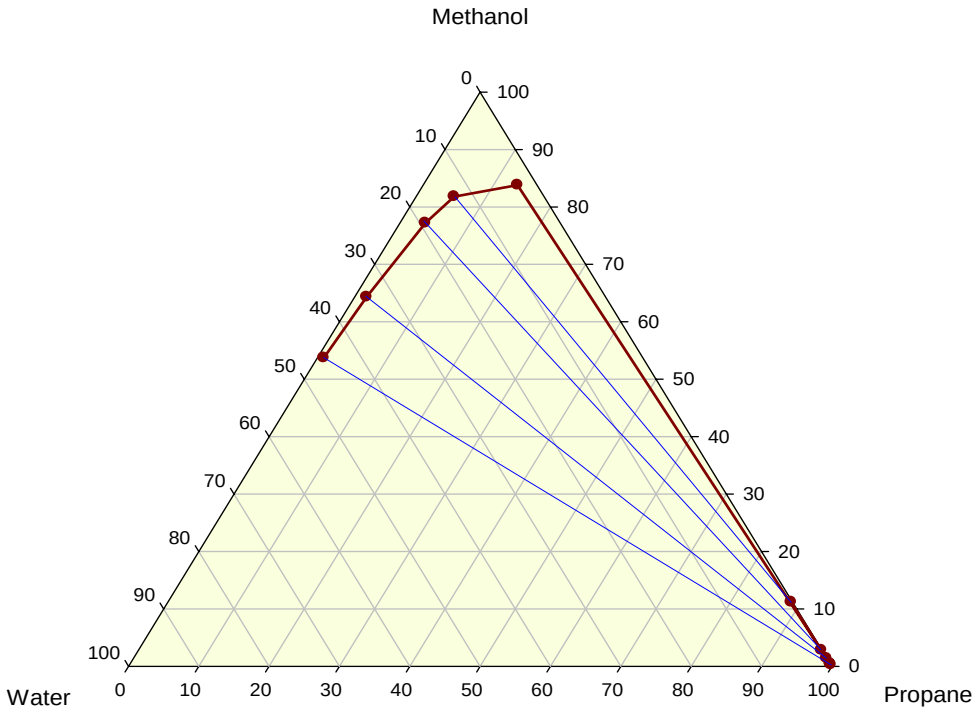


Figure 12. Phase Diagram for the Propane-Water-Methanol System at 0 C

Table 4. Solubility of Propane and Butane in Methanol

Temperature, C	Temperature, F	Propane Solubility in Methanol, mass ppm	Butane Solubility in Methanol, mass ppm
0	32	29,200	--
10	50	22,700	--
20	68	17,900	--
25	77	--	57,500
35	95	--	34,800
40	104	11,700	--

Phase and Solubility Behavior of the Propane-Water-Methanol System

Phase Behavior of the Propane-Water-Methanol System

The short communication of Noda, et al. (in Ternary Liquid-Liquid Equilibria) provides just enough data to define the basic shape of the ternary propane-water-methanol phase diagram at 0 C and 20 C. A plot of these data is shown in Figure 11, while Figure 12 shows a similar diagram at a temperature of 0 C. Noda, et al. also provide information on the solubility behavior of butane-water-methanol system; these data are shown in Figure 13.

Note that the graphs shown in Figure 11 through Figure 13 are constructed so that each side of the triangle shows the concentration of one of the constituents. The concentration scales are in mole percent and are read counter clockwise. Thus, the top of Figure 11 corresponds to a concentration of 100 percent methanol, the lower left to 100 percent water and the lower right to 100 percent propane. The blue lines are tie lines. Any mixture whose overall composition lies on the tie lines will split into two phases whose compositions are shown at the ends of the line.

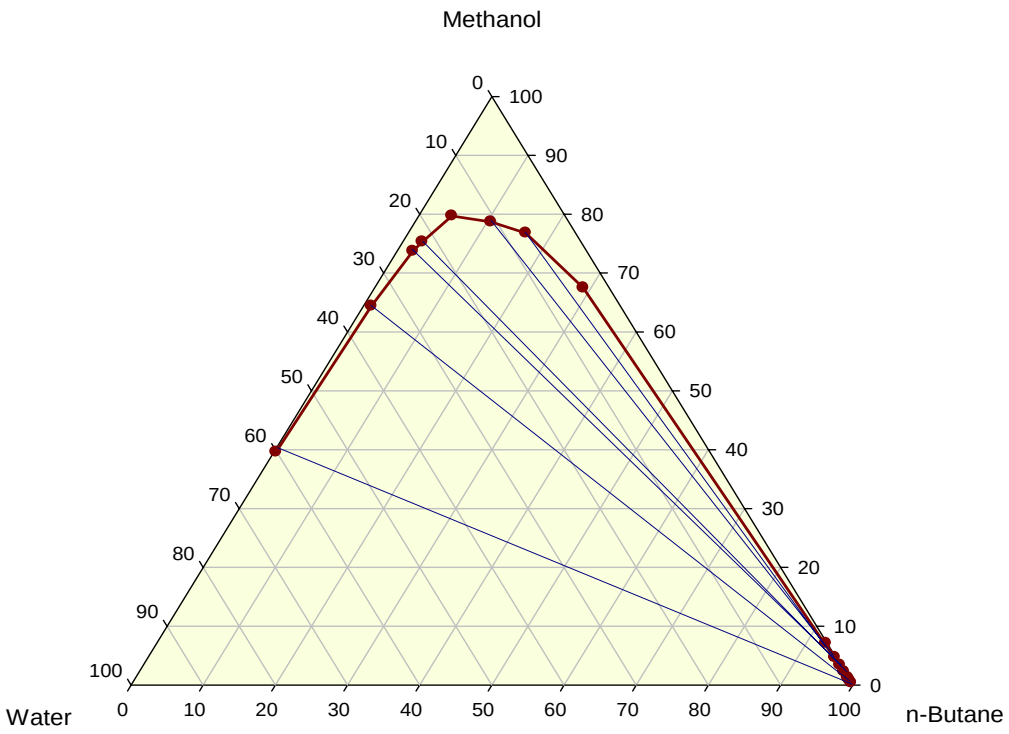


Figure 13. Phase Diagram for n-Butane-Water-Methanol System at 20 C

In the ternary propane – methanol – water system, since water is only slightly soluble in propane while water and methanol are completely miscible, whenever there is an excess of both methanol and water, two phases will be present. One phase will be mostly propane with small amounts of water and methanol and the other phase will be predominately water and methanol with only a small amount of propane. The propane rich phase, because it is less dense, will always be above the water – methanol rich phase. Figure 14 shows the extent of the partitioning of the methanol between the water and the propane-rich phases as the concentration of the methanol in the water is varied, based on both calculated results and experimental data. Note that the most of the methanol tends to be in the water-rich phase, as would be expected from the chemical similarity between these two polar substances.

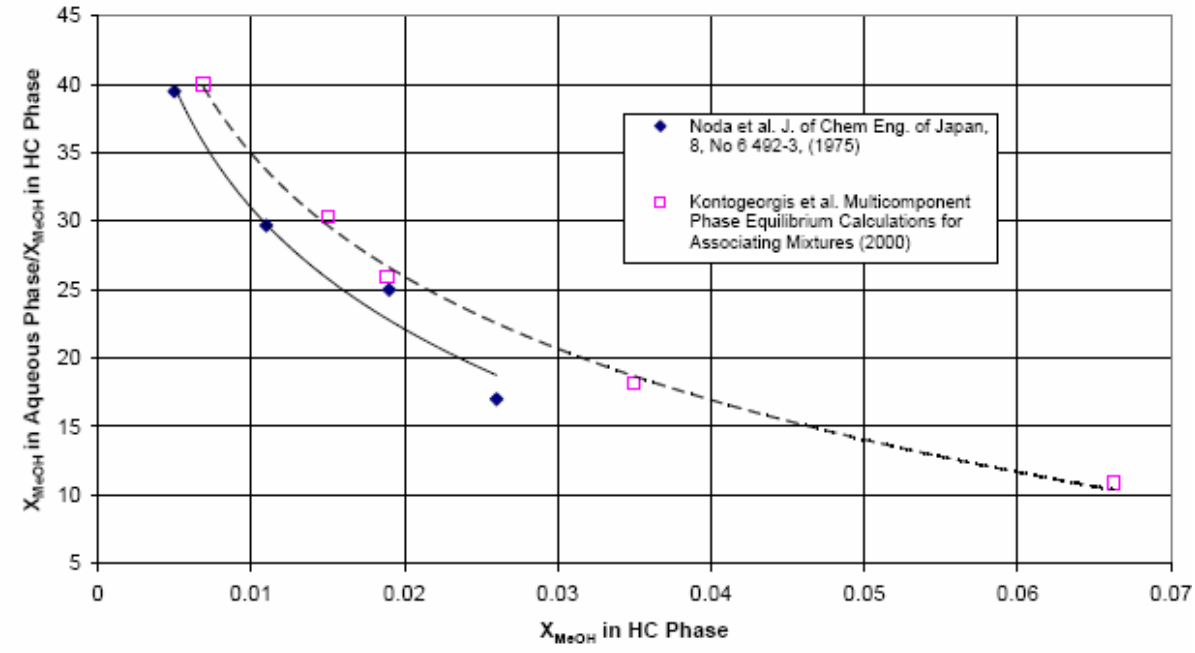


Figure 14. Partitioning of Methanol Between Water-Rich and Propane-Rich Phases (figure prepared by A. Spataru, The Adept Group)

Vapor and Liquid Composition Relationships

The relationship between the liquid composition and the vapor composition is key to the action of methanol as an antifreeze. Therefore, this relationship is explored in some depth.

General Relationship Between Liquid and Vapor Compositions

For a pure liquid, the composition of the vapor and the composition of the liquid are the same. For a multi-component system, where the attractions between molecules differ, the vapor composition is generally different from the composition of the liquid. For the case of an "ideal" solution, the vapor composition is given by Raoult's Law which states that:

$$p_i = x_i p_i^o \quad \text{where:} \quad \begin{aligned} p_i &= \textit{partial pressure of component i in liquid} \\ x_i &= \textit{mole fraction of i in liquid} \\ p_i^o &= \textit{vapor pressure of i} \end{aligned}$$

The amount of a component in the gas phase as compared to the liquid phase may be stated in terms of a ratio, usually designated by the letter K. K is defined as follows:

$$K = \frac{y_i}{x_i} \qquad \text{where:} \quad \begin{aligned} x_i &= \textit{mole fraction of i in liquid phase} \\ y_i &= \textit{mole fraction of i in gas phase} \end{aligned}$$

For real solutions this Raoult's Law does not hold and the concentration of a species in the vapor phase may be more or less than that predicted by the mole fraction in the liquid. In the case of a solution where the intermolecular attractions are quite different, such as non-polar propane molecules and polar water or methanol molecules, there is often a greater tendency of the molecules that "don't fit in" to escape; this is reflected in a vapor that is greater than would be predicted by Raoult's Law and the K ratio is greater than expected.

Mention must also be made of the special case where K = 1. In this case, the composition of the vapor is the same as the composition of the liquid. For solutions, this is the case if there is the formation of an azeotrope, a mixture that cannot be separated by vaporization and distillation.

Liquid-Vapor Composition Relationship for the for Propane-Water and Butane-Water Systems

For water dissolved in propane, the mole fraction of water in the vapor phase is larger from the mole fraction of water in the liquid phase, leading to a K ratio greater than one. Hachmuth (in "Butane-Propane News") reports experimental data for the K ratio for water vapor over propane. These data are plotted in Figure 15. As Figure 15 shows, the data are linear with temperature and can be represented by the equation:

$$K = 7.59 - 0.0880 * (T)$$

where T = temperature of the propane in degrees C

From this equation we may prepare a table of the K ratios at various even temperatures, this is shown in Table 5. Note that as the temperature decreases, the K ratio increases. This enrichment in water vapor concentration at lower temperatures exacerbates the potential for condensing and freezing of water in valves and regulators.

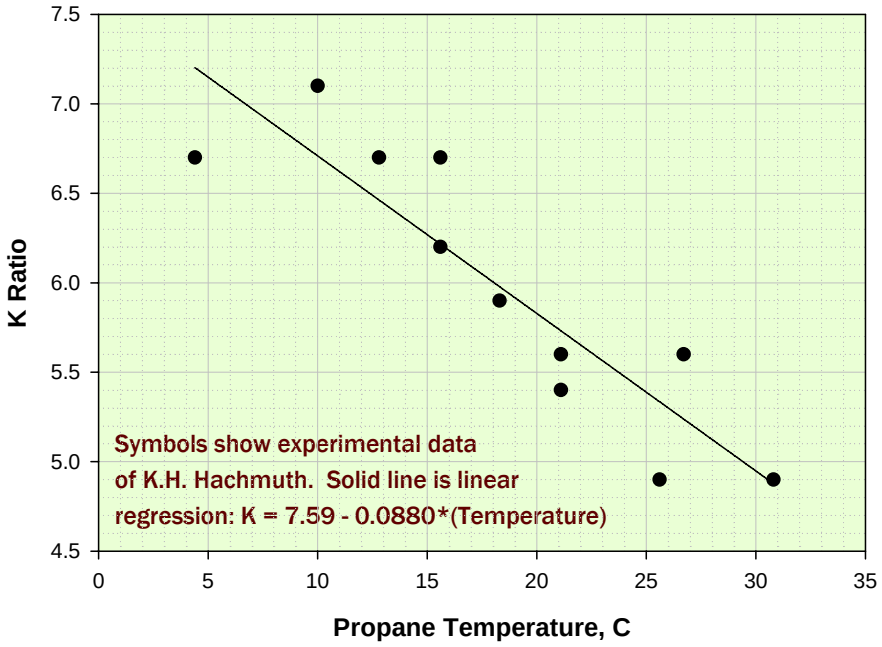


Figure 15. K-Ratio Data for Water in Propane

Table 5. K Ratio Data for Water in Propane

Temperature, C	Temperature, F	K ratio for water in propane
-30	-22	10.4
-20	-4	9.6
0	32	7.8
20	68	6.0
30	86	5.2
40	104	4.3

Folas, et al. present a graph of the mole fraction water in the gas and hydrocarbon phases for the butane-water system (Folas et al. in Application of the Cubic-Plus-Association). K ratios may be obtained from this graph and are listed in Table 6. Note that the K ratios for water in butane are larger than those for water in propane. Reamer, et al. (in Phase Equilibria in Hydrocarbon Systems) and Folas, et al. (in Application of the Cubic-Plus-Association) also present K-ratio data water in for n-butane; their data show a ratio of about 16 at 25 C (77 F).

Table 6. K Ratio Data for Water in Butane

Temperature, C	Temperature, F	K ratio for water in butane
30	86	50
40	104	36
60	140	28

Liquid-Vapor Composition Relationship for the Propane-Methanol System

No experimental K-ratio data for the methanol-propane system were located. Because knowledge of the K-ratios for the methanol-propane system are important in developing guidelines for the use of methanol as an antifreeze, we estimate the K ratio for methanol using two different methods.

The first estimate is derived from a comparison of the values for water with the values shown on the well-known K ratio correlation prepared by DePriester. Such a comparison shows that the K ratio values for water (polar, MW=18) are similar to those for ethene (non-polar, MW=28), an olefin whose molecular weight is about 1.5 times that of water. If we extrapolate from these data for water to methanol (polar, MW=32), we may surmise that the K ratio values would be similar to those for propene (non-polar, MW=42). If this is the case, we would estimate the K-ratio values for methanol would range from 1.7 at -30 C (-22 F) to 1.3 at 30 C (86 F). These estimates for K are shown in Table 7.

Table 7. Estimated K Ratio for Methanol in Propane

Temperature, C	Temperature, F	Estimated K ratio for methanol in propane
-30	-22	1.7
-20	-4	1.5
0	32	1.3
20	68	1.35
30	86	1.3
40	104	1.4

The second estimate of the K ratio for the methanol-propane system is derived from an inspection of Figure 9. The K ratio at the azeotropic composition of 6,700 mole ppm (approximately 5,000 mass ppm) methanol would, by definition be 1 because the composition of the liquid and the composition of the vapor are the same. For methanol concentrations less than the concentration at the azeotrope, this the graph indicates a K ratio of about 2; and much less than 1 for higher methanol concentrations. Note again, though, that curves shown in Figure 9 are calculated results only.

Implications for the Behavior of Propane Fuel Systems

It is useful to examine the implications of the phase and solubility behavior on the behavior of propane fuel systems in the presence of water and methanol.

Dry Fuel Systems

If the LP gas fuel is perfectly dry, then, clearly, both the liquid propane and the vaporized gas will be water free. But because the solubility limit for water in propane has not been reached, if any water or moisture is present, the liquid propane has the ability to absorb some or all of it.

Fuel Systems with Some Dissolved Water

If the liquid propane that is delivered to the distributor has some dissolved water, there are several possibilities. If the amount of water small, less than 20 ppm, the water will remain solution in the liquid, even as the propane cools to winter storage temperatures.

However, if the amount of water is greater than this, the water can come out of solution as the propane cools. Initially, this water will form small droplets, but, because the density of liquid water is greater than that of liquid propane, this water will eventually form a water layer on the bottom of the tank.

Once a water layer has formed, the diffusion of water into liquid propane is so slow that even if the propane warms or is replaced by drier fuel, the water will not readily go back into solution, but will remain as a lingering source of moisture.

If there is water in the liquid propane, there will also be water in the propane vapor. In fact, because of the K ratio, there will be a 4 to 10 times greater concentration of water in the vapor than in the liquid.

For example, consider liquid propane saturated with water at 20 C (68 F). At this temperature, about 80 mass ppm of water will dissolve in propane. This is equal to 196 mole ppm. The K ratio at this temperature is 6, so there will be 1176 mole ppm of water in the propane vapor. This is the same as 1176 volume ppm. And, although mass ppm is not generally used with gases, this would be 480 mass ppm.

If this propane vapor is cooled sufficiently, liquid water will condense. The expansion through a pressure regulator can cause this cooling, and the amounts of condensed water can be considerable. Consider a combustion appliance that uses fuel at a rate necessary to provide 100,000 Btu/hr of heat. If, as in the previous example, there are 1176 mole ppm of water in the vaporized fuel, 1 gram of water per hour is being carried with the fuel. It may be readily appreciated that if even a portion of this water condenses and freezes in a valve or regulator, blockages can occur.

Summary

In summary:

- If propane is perfectly dry, there won't be any problems.
- If the water content is very low, perhaps less than 20 mass ppm, even if the liquid propane is cold, no water will come out of solution.
- If however, the propane is saturated with water when it is warm, a) liquid water will separate out of the liquid propane is cooled, and b) the propane vapor will contain enough water that ice may form as the propane vapor expands and cools in valves and regulators.

Knowledge Gaps

Experimental Data

Additional experimental data on the propane-water-methanol system are needed to:

- Clearly define the amount of methanol that is soluble in propane at low temperatures and the nature of the propane-methanol cloud point curve. This is necessary to know under what conditions a phase separation and the formation separate methanol-rich liquid layer would occur.
- More clearly define the solubility characteristics of water in propane to which methanol has been added. We have not identified data that show if there are any interactions. Again, these data would help define the limits of both methanol and water solubility at very low temperatures.
- Provide K-ratio data for methanol in propane, particularly in the -20 to 30 C range, and determine the degree to which the K ratio for water is not appreciably affected by the presence of methanol.

Equation of State Calculations

In theory, all of the above behavior can be described by an appropriate equation of state.[*,†] However, success in formulating such a general equation of state has been mixed, though progress is being made, much of it in the post-2000 timeframe. Robinson, et al. (in Development of the Peng-Robinson Equation), Kontogeorgis, et al. (in "Multicomponent Phase Equilibrium Calculations"), Velasco, et al. (in "Dew Points"), and Joung, et al. (in "High-Pressure Vapor-Liquid Equilibrium Data") have developed equations of state that are intended to represent

[*] An equation of state is an equation which relates the temperature, density, and pressure of a fluid. Because other fluid properties can be derived from these, an accurate equation of state can be used to describe the complete phase behavior of a fluid.

[†] A good discussion of the procedures involved may be found in Properties of Gases and Liquids, Fourth Edition, Robert C. Reid, John M. Prausnitz and Bruce E. Poling (1987). See especially Chapter 8: Fluid Phase Equilibria in Multicomponent Systems, pp. 241-387.

highly non-ideal systems such as the propane-water-methanol system. Given the development of such equations, equations of state may be able to provide useful calculated results. Work is needed to:

- Identify which of the different equation of state models (there are at least six contenders) would best represent the propane-water-methanol system.
- Perform equation of state calculations for the propane-water-methanol system.
- Validate the equation of state model results with experimental data.
- Translate the equation of state results into tables and graphs that provide practical assistance to the propane industry.

Although the successful use of methanol as an antifreeze over many decades indicates that methanol works well under most conditions, more complete information is necessary to define the limits, particularly the conditions that may produce a second water- and methanol-rich phase in a tank.

Water and Methanol Content Measurement

Introduction

Water and methanol are both polar molecules that may be present in LP gas fuel in ppm amounts. Because the measurement needs are similar, and because there is some similarity in chemical response (both water and methanol contain –OH groups), the measurement of both water and methanol content measurement are discussed together in this section.

Measurement Criteria

The criteria for satisfactory water and methanol content measurement are:

- Adequate precision and accuracy in the range of concentrations commonly observed in propane.
- Freedom from interferences from other substances that may be found in propane.
- Usable in the field by propane industry personnel
- Reasonable cost.

These criteria will be re-visited in the observations and recommendations sections.

Current Status of Water Content Measurement

There are several tests for water content of LP gas in use, including the cobalt bromide, stain tube, valve freeze, dew point (chilled surface), and electrochemical tests.

There is no generally available or accepted field test for the measurement of methanol in LP gas.

Units of Measure for Water Content

Several units of measure for water content are in use. Some equivalent water content values in different units are shown in and Table 8 and Table 9 below.

Table 8. Conversion Table for Water Concentrations (Liquid Propane)

ppm (mass)	ppm (mole)	lb water/100 lb propane
41	100	0.0041
100	245	0.10
150	367	0.015

Table 9. Conversion Table for Water Concentrations (Propane Vapor)

ppm (volume) ppm (mole)	mg/L	lb/MMscf
100	0.75	47
133	1	62
213	1.60	100

Of these units, parts per million are generally in a convenient numerical range and have the advantage of being independent of the use of SI or English units. Although the use of mole ppm is more common in science, units of mass ppm are perhaps more easily visualized.

Units of Measure for Methanol Content

Some equivalent units for methanol content are shown in Table 10 and Table 11 below.

Table 10. Conversion Table for Methanol Concentrations (in Liquid Propane)

ppm (mass)	ppm (mole)	lb methanol/100 lb propane
73	100	0.0073
100	138	0.010
2500	3440	0.250

Table 11. Conversion Table for Methanol Concentrations (in Propane Vapor)

ppm (volume) ppm (mole)	mg/m^3	lb/MMscf
100	133	8.28
1000	1330	82.8
10,000	13,300	828

Measurement Range Needed

Water

The solubility of water in liquid propane is such that "wet" propane could have 500 mole ppm of water in the liquid. Given the K-ratio, this would mean about ten times that concentration in the vapor or 5,000 volume ppm.[*] So, measurements of water concentration need to cover the range of roughly 0 to 5,000 volume ppm in the vapor phase.

Methanol

The methanol treatment rate listed in RegO's *LP-Gas Serviceman's Manual*, for new tanks or tanks that have been hydrotested, amounts to about 2,400 mass ppm or 3,300 mole ppm of methanol in the liquid propane. This assumes that the tank is filled to an 80 percent level. Complete data for the K ratio for methanol dissolved in propane is not known, but may be expected to be greater than one and somewhat less than the ratio for water. Assuming a K ratio of 1.5, we would need to measure methanol vapor concentrations from zero to perhaps 5,000 mole ppm.

Sampling Issues

In this context, accurate sampling means obtaining small amounts for analysis that are representative of the entire bulk of material. In order to draw accurate and correct conclusions, a sample that is representative of the material being sampled is essential. Before we can proceed to the methods of measuring water (or methanol) content in LP gas fuel, there are sampling issues to be addressed. Some of these issues are described in an article by Falkiner (in "Liquefied Petroleum Gas").

Vapor Composition vs. Liquid Composition

Because of the differing volatilities of propane and water, the composition of the vapor is different from that of the liquid; this is given by the K ratio. Note that the K ratio varies with temperature and may not be known exactly for all LP gas compositions.

[*] Here we are speaking of mole ppm, so no conversion of units between the liquid and volume concentrations is necessary.

Example:

Consider the process of taking a small sample from a large tank of liquid propane at 20 C (68 F). At this temperature approximately 180 mass ppm (370 mole ppm) of water (see Figure 6) will dissolve in propane. The K ratio for water in propane is about 10, so we expect the vapor space to contain about 3700 mole ppm water, which is also 3700 volume ppm water. Thus, depending on whether the sample is obtained from a liquid propane stream that is totally evaporated or from a vapor space sample, the concentration of water that must be determined will be either about 180 mass ppm (370 mole ppm) or 3700 volume ppm.

Water Adsorption During Sampling

Another difficulty with analyzing propane for water content is that care needs to be taken to make sure that the sampling or inlet system is not "contaminated" with water. From the discussion above, it may be noted that the amount of water actually contained in the propane in a typical size sample container is small and the amount of water found by analysis can be affected by the water adsorbed in sample lines and in the inlet systems to analysis instruments. It is not known the degree to which methanol may be adsorbed onto the walls of sampling systems.

ASTM Methods for Sampling LG Gas and Propane

There are two ASTM methods for sampling propane, ASTM D 1265, *Practice for Sampling Liquefied Petroleum Gases* and ASTM D 3700, *Standard Practice for Obtaining LPG Samples Using a Floating Piston Cylinder*. ASTM D 1265 is fairly commonly performed, but has accuracy problems when sampling for substances with K factors greater than one.

The problem with sampling propane using ASTM D 1265 is that the propane is a liquid under pressure and that the vapor which is in equilibrium with the liquid will have a different composition than the liquid. Because sample cylinders must be filled to only 80 percent of capacity to allow room for propane expansion, some of the sample must be vented in order to maintain this level, thus resulting in a loss of volatile components. The use of outage tubes (or a valve at the bottom of the container) for reducing the fill of the sample cylinder level to 80 percent may be better, but because the vapor space is increased, there is still an error.

ASTM D 3700 is specifically designed for obtaining highly accurate samples with LP gas fuel containing volatile or "light" components. The sample equipment for ASTM D 3700 is larger and more expensive than that for D 1265, but the D 3700 equipment does allow for the accurate determination of the concentrations of the volatile components. Because of their volatility in propane solution, the measurement of water and methanol would definitely qualify as light components.

The ASTM D 3700 sampling apparatus has been criticized because it can introduce heavy ends into the propane through contact with the rubber gaskets and lubricants which come into contact with the propane in this style of sample cylinder, but if the light components are the components of interest, the use of the ASTM D 3700 procedure is appropriate.

Current Methods for Water Content Measurement

The Cobalt Bromide Test

Description

Cobalt (II) bromide ($CoBr_2$) is a green salt that is soluble in water to form a red solution. The cobalt bromide test is based on the observation that when cobalt bromide is deposited on a wad of cotton, the color changes from green to lavender to purple in the presence of water vapor. According to the Engineering Data Book of the Gas Processors Suppliers Association, the color change occurs when the relative humidity of water vapor in propane vapor is about 30 percent.

The test is performed with a stream of propane vapor at 0 C (32 F). The water content of saturated propane vapors at 0 C is 530 ppm and the water content of saturated propane liquid is 35 ppm (for a K ratio of 15). Thus, the water vapor concentration associated with the cobalt bromide color change is 30 percent of 530, or 159 ppm, corresponding to a water concentration in liquid propane of 10 ppm.

Accuracy

The cobalt bromide test is basically a go-no go test. Clearly, there is some subjectivity in observing the color change. Because the relative humidity and saturation temperatures change with temperature, it is important that the 0 C (32 F) test temperature be maintained.

Needless to say, the cobalt bromide reagent must be handled in such a manner that is it not affected by moisture from the air.

Cobalt bromide is also soluble in methanol to form a red solution (*The Merck Index*). Although specific data on the behavior of cobalt bromide upon exposure to methanol vapor was not found, based on cobalt bromide's ability to form a red methanol solution, it would be expected that cobalt bromide moisture test would also respond to methanol vapor by producing a purple-red color.

Discussion and Comments

This test is simple in concept. However, it does not provide quantitative information on water content. For about the same amount of trouble, a length-of-stain detector tube can be used to gain a more quantitative indication of water content. Thus, the cobalt bromide test is seldom used.

The Valve Freeze Test

Description

The valve freeze test is described in ASTM standard D 2713. In this method, a propane test valve is connected to a source of bulk liquid propane. The liquid is allowed to flow through a

valve with a small orifice, where the pressure and temperature drop due to flash vaporization of the liquid propane. If there is excess moisture in the propane vapor, the moisture will freeze thereby blocking the valve orifice. After some short flows to precondition the apparatus, the valve is opened and the time until the liquid flow is stopped by valve icing is timed with a stopwatch. If the time is greater than 60 seconds, the product is deemed acceptable. Figure 16 shows an example of a valve freeze test apparatus.

The freeze valve test is intended to measure the amount of water in the liquid propane. Therefore, it is best taken at the bulk tank so that there will be no sampling issues.



Figure 16. Example of a Valve Freeze Test Apparatus

The ASTM D2713 standard includes a note with data about freeze times and water content. These data are plotted in Figure 17. The plot suggests that the freeze-valve test response is non-linear.

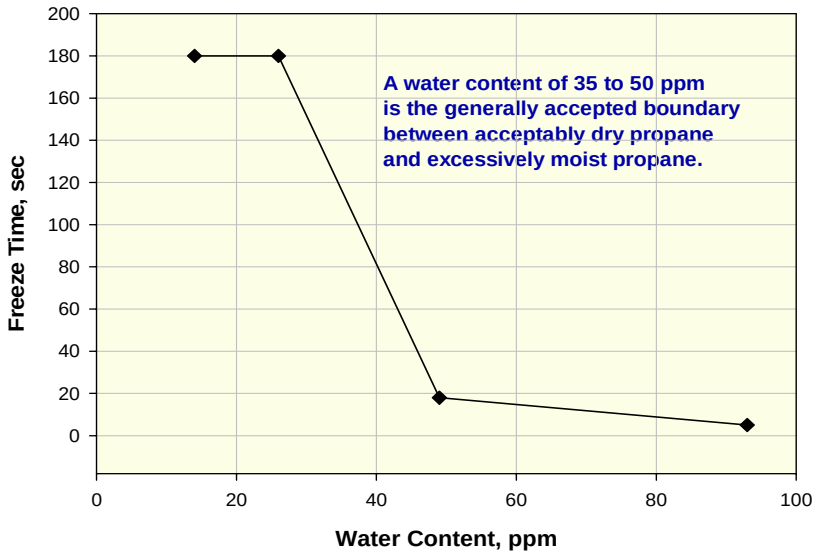


Figure 17. Plot of Freeze-Time Data in ASTM D 2713, Note 6.

Accuracy

While the concept of valve freeze test is simple, the practical application of the test can be difficult. The process is not completely controlled and is not always very repeatable. Even the

text in the ASTM standard notes that as many as eight test runs may be necessary to obtain consistent results when the flow times are less than one minute. The ASTM D 2713 standard does not include any information on accuracy, repeatability or reproducibility; and because the results are defined in terms of the test apparatus rather than in terms of water content, it is not possible to include any bias information for this test.

There are, however, more fundamental difficulties with the valve freeze test. First, although some information about the water content of the fuel may be inferred from the time to freeze, the test is basically a pass-fail test that does not provide information about the degree of saturation of the liquid LP gas fuel with respect to water content. And, while the D 2713 valve freeze test may show that a given batch of fuel requires methanol addition, the test does not provide information to allow a decision on how much methanol to add.

In addition, while there is a great deal of industry familiarity with the valve freeze test due to its long history of use, there is not a systematic body of data that supports the selection of the valve freeze test parameters and or that demonstrates the relationship of the test results to the actual water content of the fuel or to the performance of valves and pressure regulators in the field.

The amount of cooling derived from the evaporation subsequent expansion of the propane[*] in the freeze valve apparatus depends on the initial pressure of the propane, the final pressure downstream of the orifice, and the flow rate. And the tendency to freeze will be "resisted" by the heat capacity of the valve and the amount of heat transfer to the valve from the surroundings. The prior history of the apparatus may be important as it may take some time for the internal parts to completely equilibrate after being exposed to a temperature change. All these things have the potential to affect the test results, but are only imperfectly controlled in the ASTM test protocol.

Discussion

Despite the difficulties in performing the valve freeze test and despite the difficulty in relating the results to actual water content, as well as the non-linearity of response to water content, the valve freeze test has one major advantage: it mimics actual usage where the issue is the freezing of valves and regulators on liquid lines where vaporization occurs. But it remains a go-no test with poor accuracy and repeatability. And it does not directly address the formation of ice or propane hydrates in valves or regulators in vapor service. Also, the test is relatively time-consuming to run and conducting the test results in venting propane to the atmosphere, which is not desirable for safety and environmental reasons.

With regards to the use of methanol, the ASTM D 2713 specifically states that "This test method is not applicable to propane-type products containing antifreeze agents. However, the relative freeze times of such materials may be an indication of the tendency of these products to cause freezing in pressure-reducing regulators." (Standard Test Method for Dryness of Propane) This is a weak statement for an industry standard method.

[*] As would be measured in units of heat per unit of time, e.g., watts or Btu/hr.

Comments

The valve freeze test is not likely to be improved by simple changes or additions to the procedure. Instead, other methods should be sought for testing water content that are more repeatable and more accurate.

We also note the valve freeze test is also an intrinsically "messy" test that requires the release of fuel into the environment.

Length-of-Stain Detector Tubes

Description

Length-of-stain gas detector tubes contain a reagent that changes color in contact with the analyte. Figure 18 shows a length-of-stain detector tube for water. For ambient air sampling, a small hand pump is used to draw a known volume of air through the tube. For gaseous fuel sampling, a small gas sampling chamber is used to create a space from which a sample can be drawn using the pump. Procedures for using a stain tube to determine the water content of natural gas are described in "Standard Test Method for Water Vapor in Natural Gas Using Length-of-Stain Detector Tubes" (ASTM Standard D 4888).

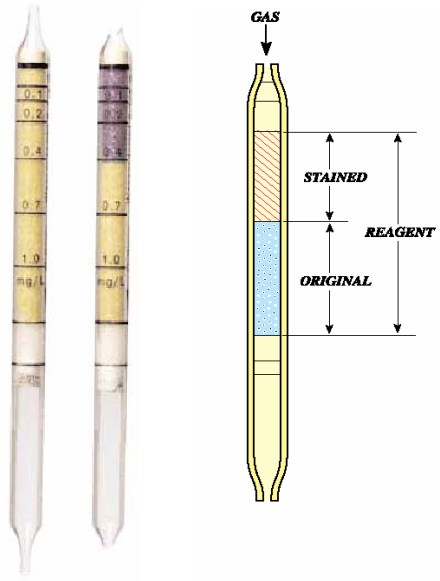


Figure 18. Length-of-Stain Detector Tube

Accuracy

The question of accuracy of stain tubes encompasses several intermediate questions:

- How accurately can the volume of sample be controlled?

- How accurately can the length of stain be judged?
- What is the variability of stain tube response due to manufacturing variations?
- How are the stain tubes affected by environmental variations?
- Are there other substances that also produce a response (interference)?

Because stain tubes have a long history of use in industrial hygiene, there is a body of work that can be brought to bear on these questions. However, it must be noted that length-of-stain tubes have different chemistries for each gas or vapor being measure, and therefore the behavior of tubes for different gases may vary as well.

The first consideration in assessing stain tube accuracy is the accuracy of the volume of gas drawn through the tube, as this is directly related to the response of the tube. The ASTM method calls for the detector tube pump to provide a sample volume that is accurate within $\pm$ 5 percent.

Another issue is the ability to read the tube accurately. Reading the tube involves fixing the boundary of the stained area, which may be indistinct, and interpolating between the legend marks printed on the tube. Both involve an error that is probably best described as a fixed fraction of the length of the tube (full scale). This may amount to perhaps 3 to 5 percent of full scale. Clearly, for low readings, this could be a significant percentage of the reading.

Overall, the ASTM standard states that the accuracy of length-of-stain detector tubes is considered to be $\pm$25 percent ("Standard Test Method for Water Vapor in Natural Gas Using Length-of-Stain Detector Tubes"). This statement is based on work done by the National Institutes of Occupational Safety and Health (NIOSH) on detector tubes that respond to analytes of occupational hygiene interest. The ASTM standard does not provide repeatability or reproducibility estimates for the water vapor test. One vendor (Draeger Safety) provides a standard deviation estimate of $\pm$15 to 20 percent for the detector tube that measures water vapor in the range 0.1 to 1 mg/L.[*]

Interferences

Compounds with hydroxyl groups are known to interfere with length-of-stain indicator tubes for water vapor. Methanol and ethylene glycol both have hydroxyl groups. One vendor provides a graph showing the extent of this interference. This graph is shown in Figure 19. Note that, 1 mg/L of water vapor is equivalent to 1360 ppm of water, so from the graph, 660 ppm of methanol would register as 1360 ppm of water.

[*] This corresponds to a full scale 140 ppm water vapor at a pressure of one atmosphere, so the standard deviation corresponds to 21 to 28 ppm.

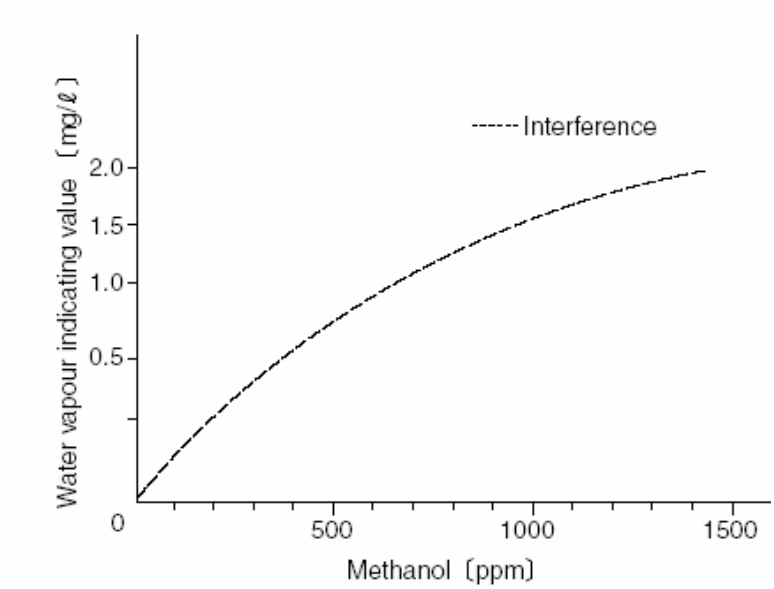


Figure 19. Extent of Methanol Interference with Stain Tube Measurement of Water Vapor

In theory, length of stain tubes could be developed with a calibration for methanol, though then water would interfere with the reading.

Sampling Issues

Stain tubes and associated hand-sampling pumps are made for ambient air sampling. The procedure for the use of stain tubes to determine the amount of water in propane vapor calls for releasing the propane vapor into a container, The sampling from the container as though it were ambient air. This has some issues.

Sample Integrity. The first issue is the classic LP gas sampling issue: unless a representative liquid sample is fed to the sample and then completely vaporized, the vapor in the container will not represent the bulk liquid composition.* It is also possible to sample vapor taken from the vapor space of the tank. In this case, an appropriate K factor must be used to relate the water content of the vapor to the water content of the bulk liquid. There is also the possibility of absorption or release of water or other substances from sampling system and/or the walls of the container.

Sample Flow Rate. The ASTM D 4888 standard calls for purging the sampling container at a rate of 500 to 2000 mL/minute. The sample pump - detector tube combination results in a withdrawal of about 150 mL/minute of gas from the sampling container. Clearly, the propane flow rate must be such that there is no possibility that air will be drawn into the container, so that air rather than propane will be sampled. The ASTM method does not call for measuring the

* Note that in constructing a test apparatus for leading a small stream of liquid propane to a needle valve and totally vaporizing the sample, we have constructed something that looks very much like the valve freeze test. Thus, it would not be surprising to have operational difficulties with this apparatus caused by blockage in the needle valve.

sample flow rate,[*] so it is left to the user to adjust a needle valve to obtain an adequate flow and to determine that there is always a positive flow out of the test chamber. Given that the flow is not visible, is it not clear how this flow rate can be effectively monitored without any instrumentation.[†]

Equipment. It is necessary to use the same brand of length-of-stain detector tube and sampling pump; work has shown that use of non-matching tubes and pumps can result in errors amounting to a factor of 2 or more (Colen, in Study of the Interchangeability of Gas Detector Tubes and Pumps). This is clearly stated in the ASTM procedure.

Temperature Effects. Two possible temperature effects are noted. First, that even though the sample volume of gas is constant, the density of gas will vary with temperature. Second, it is possible that the rate or extent of reactions of the reagents in the stain tube may change with temperature. Analyzing and correcting for the first effect is conceptually simple; the ideal gas law can be used. The second effect is more difficult to quantify. It should be noted that although temperature effects on stain tube performance have been observed (McCammon, et al., in Effect of Extreme Humidity and Temperature), the ASTM standard does not specify, place limits, or require measurement of the temperature in the chamber containing the vaporized LP gas.

There is the possibility that the temperature of the vapor in the chamber may be cold from evaporation of the LP gas. One source notes that temperatures below 0 C can cause freezing of some reagent systems (while temperatures above 40 C can cause them to evaporate) (Leichnitz, in [*] "Use of Detector Tubes"). A more detailed study by McCammon (Effect of Extreme Humidity and Temperature) tested length-of-stain detector tubes for seven gases (none of them water vapor or methanol); all showed unacceptable[‡] errors under some combinations of temperature and humidity[§], although it is not clear that all the errors were related to the environmental conditions.

Safety Issues. Finally, there are safety issues associated with using the hand sampling pump in the presence of a gaseous fuel. Clearly, care is required to avoid ignition sources, including static electricity.

Discussion

The following observations may be made on the use of length-of-stain detector tubes:

- The method is robust and generally works well.
- The equipment is relatively inexpensive and easy to use.

[*] And the inclusion of a flow meter could provide additional opportunities for water to be gained or lost from the internal surfaces.

[†] The ASTM D 1988 method for determination of mercaptans in natural gas using length-of-stain detector tubes mentions the alternative use of a polyethylene zip-lock bag as a sample container. The bag has the advantage that it is readily apparent whether or not it is under positive pressure.

[‡] In this instance unacceptable was defined as a reading that was more than $\pm$25 percent different from the actual value.

[§] Obviously, if the tube were intended to measure water vapor concentration, humidity would not be an extraneous variable.

- In general, the accuracy of length-of-stain gas detector tubes is about ± 25 percent (Carroll and Armstrong, in "Accuracy and Precision of Several Portable Gas Detectors," and in "Accuracy and Precision of Several Portable Gas Detectors: Additional Studies")
- For common length-of-stain tube chemistries, the presence of methanol interferes with the test for water.

Comments

Despite their long history of general use, length-of-stain gas detector tubes could be used with greater confidence for the measurement of water vapor in LPG. Specifically:

- A comparison should be made between results from length-of-stain detector tubes and a laboratory reference method for actual LP gas samples in the water concentration range of interest.
- Work should be performed to quantify the interference potential of methanol for actual LP gas samples.

Determination by Karl Fischer Reagent

The method of water determination by titration of the Karl Fisher reagent is a classic wet-chemistry method for the determination of water in petroleum products. This method is described in ASTM standard D 1744. Although it is not suitable for use in the field, it has been used in a number of laboratory studies of the water content of petroleum products. Not only does this method require a laboratory apparatus, the presence of mercaptans interfere with the results of this test.

Alternative Methods for Water and Methanol Content Measurement

Because none of the classic methods for water content has the convenience, accuracy and freedom from interferences needed by the LP gas industry, alternative methods of water content measurement were sought. This search builds on the previous work and report by Hutzler and Johnson (in "Investigation of Portable or Handheld Devices") for the PERC that summarizes the characteristics of a number of generic analytical technologies under consideration for the determination of impurities in propane.

Dew Point Sensors (Chilled Surface)

Description

Dew point sensors operate by chilling a surface (often with a Peltier effect* cooler) and detecting the presence of condensed droplets on the chilled surface. Generally this is accomplished by

* The Peltier effect is the creation of a temperature difference through an electric current flowing across a junction of two dissimilar materials.

making the chilled surface a mirror and using an optical beam for sensing the presence of condensation on the mirror. The use of dew point sensors was not covered by the recent PERC sensor study (Hutzler and Johnson in "Investigation of Portable or Handheld Devices").

Discussion

Dew point sensors work only with propane vapor. Thus, the water concentration in the liquid fuel would need to be inferred from the K ratio. Dew point sensors will respond to any substance that condenses at the temperature of the chilled surface. Thus, water, methanol, higher hydrocarbons, glycols, or even oil and sludge can cause a reading.

Comments

Because of the sensitivity to interfering substances, the use of dew point sensors is unlikely to be successful in LPG use. In particular, a dew point sensor cannot distinguish between water and methanol.

Dielectric Sensors

Description

Dielectric sensors work by measuring the dielectric constant of whatever substance is between the plates of a sensor that forms a capacitor. Molecules with a large dielectric constant have a large dipole moment. A larger dipole moment causes a greater interaction with the electric field in the capacitor.

Propane and other hydrocarbons have a low dipole moment and hence a low dielectric constant,[*] and water has a large dipole moment and a high dielectric constant. Because of this, a capacitance-based sensor can be developed that estimates the amount of water present based on the change in dielectric constant of the sample as measured in a change of sensor capacitance. Often, a porous material is used between the plates to "hold" the water. This type of sensor is commonly used in electronic humidity meters for application in heating, ventilating, and air conditioning (HVAC).

Discussion

Dielectric constant-based sensors are widely used for sensing the relative humidity of air. In this application they are generally quite accurate and reliable. A sensor based on the dielectric constant has been proposed as an ASTM method for measurement of water in LP gas fuel.

However, methanol also has a relatively large dipole moment and a dielectric constant-based sensor will respond to methanol vapor as well as to water vapor. For LP gas applications, this is a serious issue inasmuch as the methanol vapor would show as water vapor on the meter, leading to confusing results.

[*] The dielectric constant is also called the permittivity.

There has been research into methods of enclosing the sensor with some type of material that is more permeable to water molecules than to methanol molecules, thus reducing the response of the sensor to methanol. However, there is little data on the effectiveness of such strategies and their possible vulnerability to interferences from other substances that may be found in LP gas fuel is not known.

Comments

The dielectric constant sensor could have some utility in propane production plants, where it is certain that no methanol has been added. However, until the issue of response to methanol is resolved, the dielectric constant sensor is not acceptable for use by propane distributors and marketers.

Electrochemical Sensors

Description

Electrochemical moisture sensors contain a porous material that absorbs water; when the water is acted upon by an electric voltage an oxidation-reduction reaction occurs that can be sensed electronically. The sensor generally consists of two electrodes with a layer of phosphoric pentoxide (P_4O_{10}) between the electrodes. Phosphorus pentoxide is very hygroscopic and absorbs all the water in the gas sample. The electrodes cause electrolysis of the water; the resulting current is proportional to the moisture content in the sample gas.

Discussion

Electrochemical or electrolytic sensors have a long history of use in the natural gas industry. Because of the need to absorb the water on a solid, response is relatively slow. Generally the absorbent needs replacement or regeneration periodically. Based on the theory of operation, it is possible that the electrochemical sensor will respond to other substances as well as to water.

Comments

Electrochemical sensors are an old technology that has been eclipsed by faster and more convenient methods.

Gas Chromatography

Gas chromatography can be used as a laboratory reference method for either water or methanol. However, the expense and training required to use gas chromatography, as well as the difficulty of calibration, the need for compressed gases and for other laboratory support precludes the use of gas chromatography as a field method for the measurement of water or methanol in propane. And taking samples back to the lab requires that the sample integrity be maintained, which is not easy with ppm levels of water or methanol, both of which can readily adsorb onto the surface of the sample container.

Comments

Gas chromatography is a good laboratory reference method, but there are other methods that are more suitable for field use. The most accepted method* for the determination of methanol using gas chromatography uses an extraction process that requires a relatively large sample, up to 1 liter.

Non-Dispersive Infrared (NDIR)

Description

Non-dispersive infrared (NDIR) spectroscopy is an analytical technique that is based on the absorption of infrared light. Because different substances absorb infrared light at different wavelengths, and because the amount of absorption is proportional to the amount of substance present, this technique can be used to determine the amount of specific compounds, even in the presence of other substances, as long as the wavelengths where absorption occurs do not overlap.

An examination of the infrared spectra of water, methanol, propane, and propene indicates that there are characteristic, non-overlapping absorption bands associated with each of these substances and that therefore there is a good potential that the NDIR method could be used be used to construct a meter for the field measurement of the amount of water and/or added methanol in a gaseous propane sample. (See Figure 20 through Figure 23 – in these figures the vertical axis is the fraction of light absorbance, and the horizontal axis is wavenumber [which is the reciprocal of the wavelength], in units of m^{-1}.)

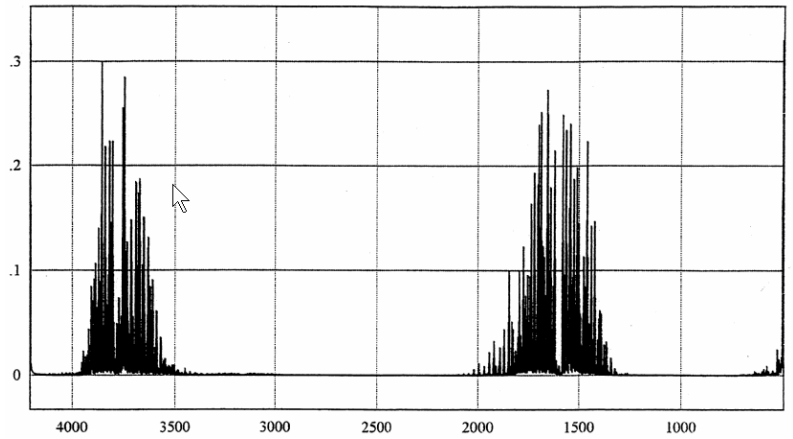


Figure 20. Infrared Spectrum of Water Vapor

* According to UOP Method 569-79 Methanol in Petroleum Distillates and LPG by Gas Chromatography.

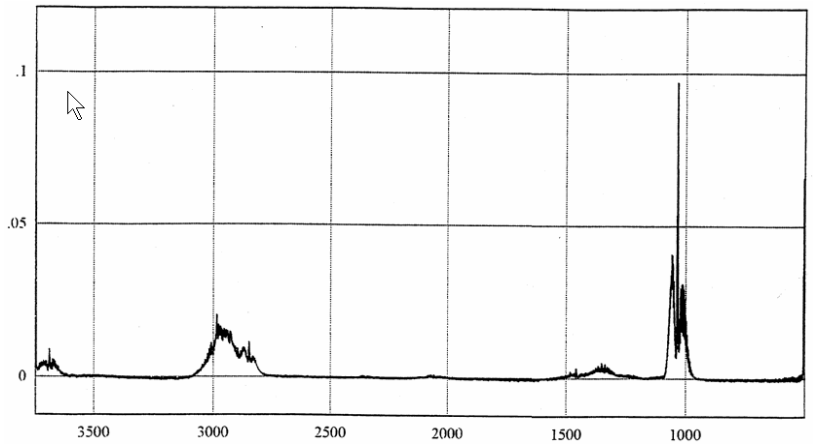


Figure 21. Infrared Spectra of Methanol Vapor

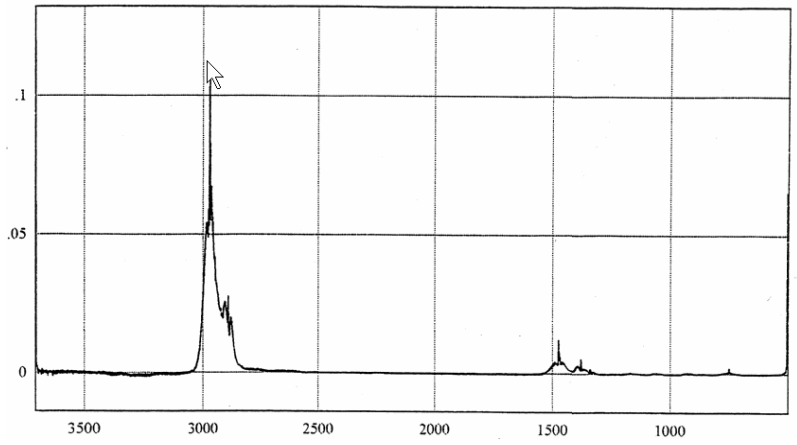


Figure 22. Infrared Spectra of Propane Gas

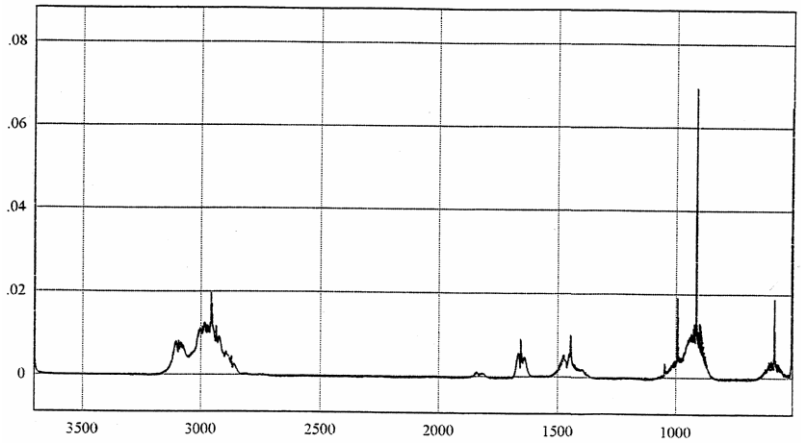


Figure 23. Infrared Spectra of Propene Gas

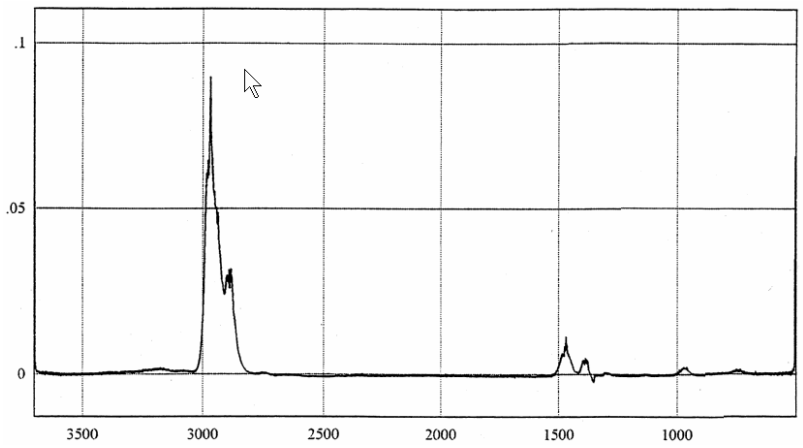


Figure 24. Infrared Spectra of Butane Gas

Discussion

In the heating, ventilating and air conditioning (HVAC) arena, small, portable instruments based on the NDIR principle have become the method of choice for making field measurements of carbon dioxide (CO_2) in the air in buildings. Handheld NDIR analyzers are available for this purpose that measure ppm levels of CO_2 with a precision of 1 ppm and $\pm$ 3 percent accuracy. These instruments are available from several vendors for a cost of less than $500. One such instrument is shown in Figure 25. Similar instruments are also used by HVAC technicians for the detection and measurement of refrigerant leaks.



Figure 25. A Handheld NDIR-Based CO2 Meter



Figure 26. Internal View of an NDIR-Based CO2 Sensor

Comparison of Water and Methanol Vapor Measurement Methods

Table 12 shows a comparison of different measurement methods. As noted in the above sections, the existing field tests for water content (cobalt bromide, valve freeze, length-of-stain tubes, and dielectric constant), are not satisfactory. Furthermore there is currently no practical field test for methanol content of propane. Thus, the development of a field test meter that could measure both water and methanol would be of great value.

Table 12. Comparison of Methods for Determination of Water in Propane

Requirement	Ideal Standard for Evaluation	Valve Freeze	NDIR	Dew-point	Stain tube	Capacitance
Accuracy of test results	Within 10 percent	0	5	5	2	5
Freedom from interference	Does not respond to methanol, glycols, or fuel impurities	1	5	1	3	1
Cost of apparatus	Less than $1,000	5	4	4	5	4
Sensitivity	Able to detect 10 ppm water in liquid propane (or equiv. in vapor)	1	5	5	1	4
Evaluation scale 0 to 5 Possible total = 20	Total:	7	19	15	11	14

The NDIR technique shows great promise not only for determination of the amount of water in propane, but also for the determination the amount of methanol in propane. Moreover the NDIR technique could be extended to the determination of water and methanol concentrations in liquid propane directly. This would avoid the need to use K-ratios for estimating the actual concentration of water and methanol in liquid propane. There would of course be the need to

define the path length, wavelength(s) and calibration curves, but this would be done during instrument design and be transparent to the user.

Recommendations

Advances in optical and electronic technologies have made feasible the development of an NDIR-based instrument that would allow the measurement of ppm-levels of both water and methanol in the field. Based on experience with carbon dioxide meters for HVAC applications, it is believed that such a meter would ultimately cost about $500.

The availability of such a meter would enable the LP gas marketers/retailers and others to not only know the water content of their fuel, but also know whether or not methanol had been added, and if so, how much. This information is key to preventing and controlling fuel problems; without this information we lack the ability to make rational decisions about fuel acceptability and treatment.

Knowledge Gaps

Clearly the biggest knowledge gap is the lack of an accurate, practical, and reliable field method for measuring the amount of either water or methanol in propane fuel.

The NDIR method shows promise and the development of the NDIR technique for the determination of the methanol content of propane is recommended. Algorithms need to be developed that relate the amount of water and methanol to the optical absorption at key wavelengths.

In addition, because length-of-stain tubes offer convenience at low cost, they will undoubtedly continue to be used and therefore more should be done to quantify the effects of methanol on the reading for water vapor, as well as to qualify their accuracy with LP gas fuel and their susceptibility to interference from methanol.

It is also recommended that measurements be made to better quantify the relative concentrations of methanol in the propane liquid and propane vapor (K-ratio).

Much work might be done with the valve-freeze test to better control the test conditions in the hope of reducing the variability of the test and to account for the possible presence of methanol. However, considering the magnitude of the effort required and the likelihood that the valve-freeze test will never provide more than a crude indication of water content, resources are better directed towards the NDIR test that has the potential to provide both water and methanol content quickly and accurately.

Methanol Impact on Materials

Background

Water can be introduced into LP gas fuel due to shortfalls in the refining process, as contamination while in the distribution system, or by improper cleaning and drying of tanks and vessels after inspection or hydrostatic pressure testing.[*] Methanol is often added to LP gas fuel as insurance against icing due to water contamination. However, there is the concern that the presence of too much dissolved water and methanol, either in solution or as a separate water-methanol layer, can lead to corrosion of tanks and equipment.

Little direct information was found in the literature on the corrosion susceptibility of carbon steel tanks when water or both water and methanol are present in LP gas fuel. Because most propane tanks are made of carbon steel, the discussion starts with the effect of water and water in methanol on carbon steel, then considers effects on aluminum and other metals, and then considers effects on polymeric materials.

Corrosion of Steel

Oxidation Corrosion

Corrosion Mechanism

When steel tanks, which consist of about 98 percent iron, are exposed to water and oxygen, they will corrode by the following reaction:

$$4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3 \downarrow$$

This reaction shows iron combines with water and oxygen producing ferric hydroxide, an insoluble red-brown corrosion product. The source of the water could be water dissolved in the fuel and the source of the oxygen could be residual air in the tank, oxygen dissolved in the LP gas fuel[†] or oxygen dissolved in any added methanol. If there is an opportunity for the corrosion product to dry out, such as during tank cleaning or purging, the ferric hydroxide can dehydrate and form the common red-brown iron oxide known as hematite, Fe_2O_3. The reaction for that process is:

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

[*] The "Good Practices for the Care and Custody of Propane in the Supply Chain" document, PERC Docket 11352, summarizes proper handling procedures for propane.

[†] Because of the way LP gas fuel is made and handled, it is unlikely that it will contain dissolved oxygen. However, this possibility is included for the sake of completeness.

The major variables that determine the severity of corrosion of the steel from this reaction are the water and oxygen concentrations, the temperature, and the electrical conductivity of the liquid, the latter being particularly increased by the presence of dissolved salts.

For propane tanks, the amount of internal tank corrosion resulting from this reaction will depend on the amount of water and oxygen present inside the tank. Because water and oxygen are consumed during the corrosion process, the corrosion reaction tends to be self limiting. However, the supply of water will be replenished if propane with dissolved water is added and the oxygen supply could be replenished if the tank is exposed to the air. In addition, if methanol is added, the methanol may contain dissolved water and/or oxygen.

Amount of Corrosion

We know from studies conducted on steel water tank exposed to aerated water[*] that the corrosion rate of steel will range from 5 to 12 mils[†] per year. (NACE Corrosion Engineer's Reference Book) Even at this rate, a tank with a wall thickness of 125 mils (1/8th inch) will last from 10 to 25 years before wall perforation occurs.

In the case of LP gas tanks, we can make some observations. Both water and oxygen are required for the corrosion reaction. And both can dissolve to some extent in propane. Water is miscible with methanol, and at 25 C oxygen is soluble in methanol to the extent of about 400 mole ppm (Kretschmer, et al., in Solubility of Oxygen and Nitrogen) or 400 mass ppm.[‡]

Example:

Consider a 250 gallon propane tank filled to 80 percent of capacity with propane to which methanol has been added. This is 200 gallons of propane, or 381 kg of propane. If there is 200 mass ppm of water dissolved in the propane, there are 76 grams of water in fuel in the tank.

As to the oxygen, if the tank is vacuum purged and considering that the propane refining and handling process does not lead to any significant amount of oxygen dissolved in the propane, the only oxygen present may be that dissolved in the added methanol. If methanol is added at a rate of 600 mass ppm (which is 229 grams of methanol for this amount of propane), and the methanol is saturated with oxygen, this will be about 90 mg of oxygen.

Thus, we can conclude that the rate of corrosion from this mechanism will be limited by the amount of oxygen rather than the amount of water. Each time the tank is filled with methanol treated propane, the oxygen will be replenished by this amount. However, the overall amount of corrosion is small. Continuing the preceding example calculation:

If the internal surface area of a 250 gallon tank is about 20,000 square inches, and the density of steel is 129 grams per cubic inch, the removal of even a 1 mil thickness over this surface area due to corrosion would amount to the removal of about 2,500 grams of steel.

[*] If the water is aerated, the supply of oxygen is limited only by the solubility of oxygen in water and is never depleted.
[†] A mil is 0.001 inch.
[‡] By coincidence the molecular weights of oxygen and methanol are the same, the values are numerically equivalent.

Even without considering the stoichiometry of the corrosion reaction, it may be appreciated that this is a small amount and that the corrosion from the oxygen in the methanol would not be significant.

Corrosion in Tanks with Water/Methanol Bottoms

If a propane tank has a water-rich or methanol-rich layer at the bottom there can be corrosion from contact with liquid methanol and water.

The corrosive effect on pure methanol on carbon steel depends on the water content. One source indicates that corrosion of steel by methanol is observed when methanol contains more than 0.2 percent water. (Sakakibara et al., in "Corrosion of Iron in Anhydrous Methanol")

Some insights into this situation may be gained from a consideration of the corrosion of carbon steel exposed to gasoline-methanol fuel blends. The Steel Tank Institute conducted a study to determine the effects of such gasoline-methanol fuel blends on the carbon steel (Geyer in "Compatibility of steel with oxygenated fuels"). Different fuel blends were used and some of the blends contained sufficient amounts of water to produce a phase-separated fuel. In the study, plain and welded panels were immersed in each of the test solutions for up to 24 weeks and the corrosion rates were monitored. These rates are listed in Table 13. In this test even the highest corrosion rates are too low to be of concern.

Table 13. Corrosion Rate Determination Using Electrochemical Methods

Gasoline, vol. %	Methanol, vol. %	Water, vol. %	Corrosion Rate, mil/yr
85	15	Traces	0.0180
50	50	Traces	0.0220
0	85	15	0.0071
0	85	15	0.0031
0	85	15	0.0034

Stress Corrosion Cracking of Steel

Two studies (Capobianco, et al., in "Corrosion Behaviour and Stress Corrosion Cracking" and Kefferstein and Jartoux in "Stress Corrosion Cracking of Mild Steels") have shown that mild carbon steel can crack when exposed to methanol containing low concentrations of water, between 0.05 percent to 1 percent. This behavior was found only in methanol and not for other alcoholics. The cracking was exacerbated in the presence of formic acid (a degradation product of methanol) when its concentration was greater than 25 to 50 ppm. Cracking was observed to occur in a wide variety of mild steels, with and without weldments, suggesting that changes in the metallurgical structure or chemical composition of the steel associated with welding were not factors in their susceptibility to cracking.

The cracking mechanism was thought to be due to a destabilization of the passive film on the steels when exposed to methanol containing water between 0.05 percent and 1 percent water (Kefferstein and Jartoux in "Stress Corrosion Cracking of Mild Steels"). The presence of residual stresses in the steel was still considered necessary for the cracking to occur. It was shown that the passivation regions were more stable on steels when the water content in methanol was either less than 0.05 percent or greater than 1 percent. No explanation was provided as to why only this particular water concentration range would lead to a destabilization of the passive film. However, the dependence on water concentration indicates that surface treatments to the tank and/or corrosion inhibitors could be effective in reducing any corrosion damage to the tank.

Corrosion of Other Metals

Many literature sources stated that methanol can cause severe corrosion of metals such as copper, magnesium and aluminum (Effects of the Alternative Motor Fuels Act; Safe Operating Procedures for Alternative Fuel Buses). Methanex, a large methanol producer, has recommended to not use copper alloys, zinc (including galvanized steel), aluminum or plastics for contact with methanol-water solutions ("Technical Information & Safe Handling Guide for Methanol").

Some LP gas cylinders, particularly those used on forklift trucks, are aluminum. According to DOT requirements* these tanks are made from a 5154 aluminum alloy. Information on this alloy in the Corrosion Survey Database indicates that at a concentration of 100 percent methanol with a temperature above 65 C (150 F), the corrosion rate will be greater than 50 mils per year. This is considered severe. At lower methanol concentrations and temperatures the database lists a corrosion rate of less than 20 mils per year, which is still considered moderate corrosion. No data were found on the effects of the much smaller methanol concentrations that may be present in liquid propane when methanol is used as an antifreeze additive.

Polymers

No information was located on the effect of methanol-containing propane on common elastomers. However, there have been extensive studies of the effect of gasoline-methanol mixtures on elastomers. Abu-Isa (in Effects of Methanol/Gasoline Mixtures on Elastomers) summarized these effects for a wide variety of polymers and was able to explain this information in terms of a solubility parameter concept. This method appears to have applicability for assessing the effect of propane-methanol mixtures on elastomers.

Discussion

Available information indicates that small amounts of methanol dissolved in propane will have a minimal effect on the corrosion of carbon steel propane tanks.

* As listed in 49CFR 178.68(b).

If propane tanks have a separate layer of water/methanol at the bottom, there is cause for concern. Corrosion rate data for industrial methanol storage tanks indicate that if the water content can be kept below 5,000 ppm or above 1 percent, stress corrosion is minimized. If large amounts of methanol are added to propane and a water-methanol layer is formed, it may be possible that the amount of water in methanol could be in the range of concern. Further investigation of this situation is warranted, though the prevention of water-methanol layers from forming at all is undoubtedly the first priority.

The issue of the presence of corrosion products at the bottom of the tank is not addressed in this report. This could be important if the corrosion debris interfered with the proper operation of hoses, filters, valve, or pressure regulators.

Knowledge Gaps

Corrosion is an old topic and much is known about what will happen to various materials under various conditions. But if the conditions are not known, good predictions cannot be made.

One of the main knowledge gaps is knowledge of the conditions inside propane tanks of all sizes: Is there ever a water layer? Is there ever a water-methanol layer? Is there rust? Is there other "stuff"? Anecdotal information indicates that such situations are can occur, but their true prevalence is unknown.

And while there are corrosion data for steel in contact with water and methanol, no corrosion rate data could be found for the propane-water or propane-water-methanol system. Nor do we know if there are corrosion inhibitors that can resolve corrosion problems that may exist.

In addition, there is a lack of data on the corrosion rates of aluminum for propane with water and methanol levels commonly seen in the field. This lack includes information on the possibility of stress corrosion cracking.

Methanol Impact on Vaporization

LP gas fuel must generally be vaporized before it is used. So the question arises of whether or not the addition of methanol affects the vaporization process. Two aspects of that process are considered here: the vaporization rate and the vapor composition.

Vaporization Rate

The vaporization rate may be defined as the mass of LPG vaporized per unit time. Because the vaporization rate would depend on the scale of the operation, it makes sense to normalize the vaporization rate in terms of some basic unit, such as unit mass or unit surface area.

The vaporization rate is controlled by several factors.

1. Liquids with higher vapor pressures vaporize more rapidly.
2. Heat must be supplied for vaporization. Therefore the vaporization rate is limited by the transfer of heat to the liquid surface. This is in turn affected by the thermal conductivity of the liquid, the amount of liquid mixing through convection, and, in the case of a tank, container or a piece of equipment, the amount of heat transferred through or from that tank, container or equipment.
3. The vapor must be removed from the liquid surface, either by diffusion or by convection or both.
4. The geometry of the equipment and the level of the liquid in the tank will affect the transfer heat and the flow patterns.

It may be appreciated that these quantities may change with time.

Because methanol is present in propane only at ppm level and because the K-ratio for methanol is close to 1, the effect of methanol in the vapor pressure is estimated to be negligible. Likewise, although the greater volatility of water vapor must enhance the total pressure to a very small degree, this effect is negligible and the overall rate of fuel vaporization will not be changed.

Vapor Composition

Initial Draw of Fuel Vapor

Consider the case where vapor is withdrawn from the tank. Because the K ratios of water and methanol are greater than one, the first vapor removed from a tank of LP fuel is expected to be enriched in water and/or methanol. Moreover, because the K ratio for water is greater than that for methanol, as evaporation of liquid propane proceeds, the water will be removed from the propane liquid faster than the methanol. This means it is important to have sufficient methanol in the liquid propane initially.

As a limiting case consider a tank of propane that is saturated with water at 20 C (68 F). This fuel would have about 140 mass ppm water. Consider also that the propane has been treated with methanol at the rate of 1 pint per 100 gallons, giving about 2400 mass ppm of methanol. Assuming that the K ratio for water is 15 and that for methanol is 1.5, this would lead to 2,100 volume ppm of water and 17,000 volume ppm of methanol in the initial draw of vapor.

This would lower the calorific value and the Wobbe Index of the fuel slightly. It is not likely that this difference would be noticed.

Final Draw of Fuel Vapor

Clearly as vapor is withdrawn, the water and methanol in the bulk liquid will be depleted, and the final draw of vapor will be nearly all LP gas fuel.

Liquid Withdrawal

If liquid LP gas fuel is withdrawn and then completely vaporized the composition of the vapor will match the bulk of the fuel. The exception would be if sufficient water and methanol are present to form a separate liquid layer at the bottom of the tank. In this case, the "fuel" being withdrawn from that layer would consist of a non-flammable (or barely flammable) mixture of water and methanol. Note that depending on the volume of the water-methanol phase and the location of a dip tube in the tank, this mixture may or may not be supplied during the draw of fuel from the tank.

Knowledge Gaps

A rigorous treatment of vaporization rate would require information on the exact vapor composition for a range of liquid compositions and temperatures. Such data would be the input for performing quantitative vaporization calculations, such as commonly performed for chemical engineering process analysis. As has been discussed in the physical chemistry section, our knowledge is limited for the propane-water-methanol system. Nor are data available that delineate the conditions necessary for the formation of a separate water-methanol liquid phase.

Nonetheless, this preliminary analysis indicates that the effect of methanol on fuel vaporization will not be significant. The long use of methanol as an antifreeze without significant fuel vaporization issues supports this conclusion.

Guidelines for Use of Methanol in LP Gas

Industry practice for many years has included the use methanol as an antifreeze for propane. Generally the methanol is added by propane marketers, but it is sometimes added by propane producers and/or distributors. Because the addition of methanol is not required to be indicated in the invoice or bill of lading, and because there is no practical field test for methanol concentration of LP gas fuel, it is possible that methanol may be added by more than one party in the supply chain, each party being unaware of the duplication. Thus, there is a need for:

1. Improved industry practices to administratively track methanol addition, such as the addition of a field in the bill of lading for methanol addition.

2. A field method for the determination of methanol concentration. The optical method discussed earlier shows promise as a field instrument that distributors can buy and use, and is recommended for development.

Existing Guidelines

Although the use of methanol as an antifreeze in LP gas fuel is common, specific guidelines for the criteria for addition of methanol as an antifreeze in LP gas fuel and the amounts of methanol to use have proven to be elusive. Standard industry references, such as the Gas Processors Suppliers Association *Engineering Data Book*, the *Handbook of Butane-Propane Gases*, the Liquefied Petroleum Gas chapter of the ASTM Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing, the *Liquefied Petroleum Gases* book by Williams and Lom, and PERC's *Good Practices for the Care and Custody of Propane in the Supply Chain* may mention the additional of methanol to LP gas fuel, but do not provide guidance as to when and how much methanol to add.

RegO®LP-Gas Serviceman's Manual

One industry guide, RegO's® LP-Gas Serviceman's Manual recommends the addition of 1 pint of methanol for each 100 gallons of tank capacity to new tanks, or newly hydrotested tanks. Based on an 80 percent fill for the tank, this would be 2,420 mass ppm of methanol. If the methanol were added based on the propane volume rather than the tank volume, the rate would be 1960 mass ppm. This recommendation is based on tests performed in the 1930s using LP gas containing water vapor and regulators placed in a refrigerated cabinet ("Freezing of Regulators", Buttner). It was reported that the addition of one pint of anhydrous methanol per 100 gallons of tank capacity was found to "give very satisfactory results."

Note also that for new or newly tested tanks that have been vacuum purged, the addition of methanol should be unnecessary unless the propane supply is known to have a water concentration that presents freezing problems.

Fisher Controls LP-Gas Serviceman's Handbook

Another industry guide, the Fisher Controls' LP-Gas Serviceman's Handbook, states that when a tank or container is placed into service, water should be "neutralized" by adding pure methanol according to a table that shows the "Rule of Thumb" amount of methanol to add. According to this table one gallon of methanol should be used for each 1000 gallons of tank capacity. (Although one line in the table indicates a treatment rate of 1 pint of methanol for a 150 gallon tank.) Based on an 80 percent fill for the tank, this would be 1570 mass ppm of methanol. If the methanol were added based on the propane volume rather than the tank volume, the rate would be 1260 mass ppm.

ASTM D 1835 Standard

The most recent edition (2005) of the ASTM for the standard specification for propane contains a footnote X1.1 to the effect that "During short-term upsets in production, or inadvertent contamination by trace water during storage or distribution, addition of 50 ppm methanol has proven to be acceptable to prevent valve freezing in normal applications. For guidance, based on historical experience and phase separation data, the maximum cumulative addition should not exceed 200[*] ppm by volume."[†]

The methanol concentration recommendation in Note X1.1 appears to be based primarily on the experience and opinions of ASTM committee members rather than on data submitted to ASTM.

Recommended Guidelines

Ideally, recommended guidelines for methanol use would be based on an accurate thermodynamic model of the propane-water-methanol ternary system that was verified by experimental data. Although modeling has advanced greatly in recent years, such results were not available. Therefore two rationales for recommended methanol use guidelines have been developed using available data and assumptions about the behavior of the system.

Rationale for Recommended Guidelines – Method I

Summary

One rationale for preparing guidelines on the amount of methanol that should be added can be summarized as follows:

1. Consider the amount of dissolved water in liquid propane fuel.
2. Look at the K ratio for water to estimate the concentration of water in fuel vapor.

[*] Note that 50 ppm by volume is equivalent to 80 mass ppm; 200 ppm by volume is equivalent to 315 mass ppm.
[†] This footnote first appeared in the D 1835-03a edition issued in 2003 and is found in the D1835-05 edition issued in 2005.

3. Assume that there should be the same mass concentration of methanol vapor as water vapor so that if the vapor is cooled and the water and methanol vapor are condensed, a 50-50 methanol-water mixture is obtained.

4. Consider the K ratio for methanol to obtain the methanol concentration in the liquid fuel that will provide needed amount of methanol in the vapor.

Considering each of these points in more detail:

Amount of Dissolved Water

The amount of water dissolved in the liquid propane is not usually known. As a conservative assumption, we assume that temperature is 10 C (50 F) and the propane is saturated with water. This would result in a concentration of water in liquid propane of about 100 mass ppm. A temperature of 10 C is chosen as a worst case temperature because the solubility of dissolved water in propane increases rapidly with temperature. We also assume that there may be 10 degrees C (18 degrees F) cooling of the gas associated with the reduction in pressure at the regulator that at temperatures above 0 C (32 F), any condensed water will not freeze.

Amount of Water in Vapor Phase

The K ratios for water are reasonably well known from the work of Hachmuth (Dehydrating Commercial Propane) (See Figure 15). If we assume that that the fuel temperature is 10 C, The K ratio would be about 7, leading to a concentration of water in the vapor phase of about 700 mass ppm.

Amount of Methanol in Vapor Phase

The properties of methanol as an antifreeze are such that a 50 percent solution of methanol and water will not freeze until -54 C (-64 F). (*Handbook of Chemistry and Physics*) In order to have an amount of methanol in the vapor phase equal to the mass of water in the vapor phase, 700 mass ppm of methanol vapor is required.

Amount of Methanol Needed in Liquid Fuel

In order to determine the amount of methanol required to be dissolved in the liquid fuel to result in 700 mass ppm of methanol in the vapor phase, it is necessary to consider the K ratio for methanol.

Unfortunately, there are no experimental data available that provide the K ratio for methanol in propane. Based on the discussion of Table 7, this K ratio may be estimated to be 1.5. Thus, according to this analysis, about 470 mass ppm of methanol in the liquid would be required.

Additional insight can be gained by defining two parameters, $S_{m/w}$ and $K_{m/w}$. $S_{m/w}$ is defined as the ratio of solubility of methanol in propane divided by the solubility of water in propane. $K_{m/w}$ is defined as the K ratio of methanol divided by the K ratio of water. As long as the product of these two terms is greater than one, then we can be assured that the sufficient methanol will be present to protect the system from freezing.

Rationale for Recommended Guidelines – Method II

Summary

This rationale may be summarized as follows:

1. Consider that the liquid propane is saturated with water when it is warm.
2. Assume that the liquid propane then cools greatly and the water comes out of solution and forms a separate layer.
3. Provide enough methanol that the liquid water that separates has at least 50 percent methanol and therefore will not freeze.

Amount of Water in Propane

In this analysis we assume that the propane became saturated with water when the temperature was 40 C (104 F). This would result in a concentration of water in liquid propane of about 380 mass ppm.

Amount of Water that Separates

We then assume that the propane cools to -40 C (-40 F), where the solubility of water in propane is only about 20 ppm. Thus, 360 ppm by mass of water would come out of solution.

Amount of Methanol Needed

If we want this separated water to be protected from freezing by an equal mass of methanol as an antifreeze, we need to ensure that at least 360 mass ppm of methanol leaves the propane-rich layer and enters the water-rich layer.

For this purpose we can draw on the partitioning data shown in Figure 27, taken from Voutsas, et al. (Prediction of Phase Equilibria). Recalling 100 mole ppm equals 73 mass ppm (see Table 10), Figure 27 shows that a when the concentration of methanol in the propane-rich phase is less than 7,500 mass ppm, the $K_{methanol}$ ratio is 40 or more, meaning that the concentration of methanol in the water-rich phase is 40 times that in the propane-rich phase.

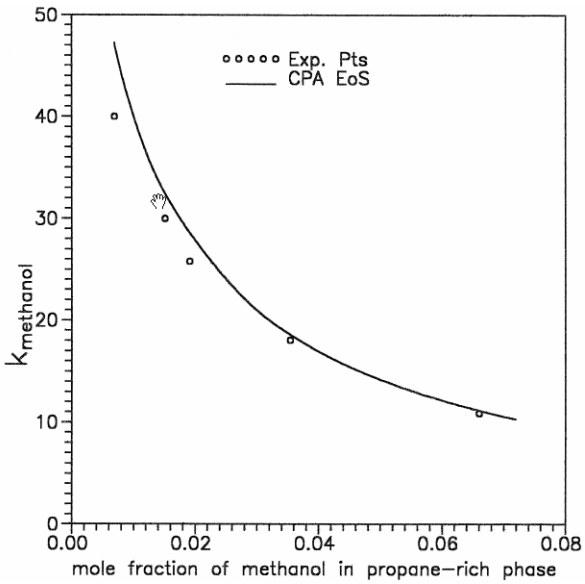


Figure 27. Distribution of Methanol Between Water-Rich and Propane-Rich Liquid Layers

Assuming that this ratio is 40, and realizing that some methanol remains in the propane-rich layer, about 200 ppm of methanol is necessary in the propane. However, there is also a vapor space, and methanol vapor is present in the vapor space as well. Given the relative masses of liquid and vapor (the mass of vapor is about 100 times less than the mass of liquid), the amount of methanol in the vapor phase is small and can be neglected.

Discussion

These two analyses predict requirements of 470 and 200 mass ppm of methanol respectively. Given that we want a "safety margin" of perhaps 50 percent, 600 mass ppm of methanol would seem sufficient. This is about one fourth the amount recommended in the RegO's *LP-Gas Serviceman's Manual* for treatment of new tanks or tanks that may have recently been hydrostatically tested and incompletely dried. Note also that for new or newly tested tanks that have been vacuum purged, the addition of methanol should be unnecessary unless the propane supply is known to have a water concentration that presents freezing problems.

Alternatives to Methanol

Properties Needed for an Effective Antifreeze Agent

Consider first the properties of methanol. Methanol is miscible with water, and when mixed with water it lowers the freezing point to -40 C (-40 F) or less and is therefore an effective

antifreeze. Because methanol has a relatively low molecular weight and volatility, it tends to "follow" the propane vapor, so it has good operational qualities. It is relatively inexpensive. Because of its long history of use, there is considerable industry familiarity with its action and limitations.

Although pure methanol is slightly acidic, corrosion from methanol at commonly used ppm levels is not a significant issue. (Although if a separate water – methanol phase forms, there can be corrosion as discussed in Section 0.)

Possible Alternative Antifreeze Agents

A search was made for alternative antifreeze agents. All chemical compounds were identified that have a boiling point of 80 C (176 F) or less, no chlorine or nitrogen, and a dipole moment greater than 0.5.[*] These compounds are listed in Table 14, in order of boiling point. Propane and water are also listed for comparison. Considering the volatility and solubility data listed in Table 14, it is possible that acetone and tetrahydrofuran could be effective antifreeze agents. But, the antifreeze agent must not react with the mercaptans used as odorants. Ketones (including acetone) and esters (including methyl acetate) have the potential for reacting with mercaptans, and so must be eliminated. Although it is possible that tetrahydrofuran could be an effective antifreeze, more information is needed about its mutual solubility with water and propane.

[*] The dipole moment is a measure of how polar the molecules are. Because water is polar, molecules that do not have some polarity, as indicated by their dipole moment, are unlikely to show significant water solubility.

Table 14. Possible Antifreeze Agents

Candidate	MW	Boiling point, C (F)	Dipole moment, μ/D	Solubility in water, g/100 g	Solubility in HC, g/100 g	Comments
Propane	44	-42 (-44)	~0	~0	miscible	For comparison.
Dimethyl ether	46	-25 (-13)	1.30	71	7[1]	Used as propellant for aerosol cans
Furan	68	31 (88)	0.66	no	?	Low solubility.
Diethyl ether	74	34 (93)	1.15	8.4	Miscible[1]	Low solubility. Only 1.2% water dissolves in ether.
Methylal dimethoxymethane	76	42 (108)	0.7	29	Soluble[2]	Little relevant data.
Acetone	58	56 (133)	2.88	miscible	?	Possible.
Methyl acetate	74	57 (135)	1.72	24	Miscible[3]	Possible.
Tetrahydrofuran	72	65 (149)	1.75	miscible	miscible	Possible.
Methanol	32	65 (149)	1.7	miscible	?	The status quo.
Ethanol	46	78 (172)	1.69	miscible	limited	Somewhat less corrosive than methanol. Also less volatile.
Methyl ethyl ketone	72	80 (176)	2.78	28	?	Limited volatility
Water	18	100 (212)	1.8	miscible	~0	For comparison.

[1] "Dimethyl Ether and Other Oxygenated Fuels for Low Emissions Diesel Engine Combustion."
[2] "Oxygenates for Advanced Petroleum-Based Diesel Fuels."
[3] No data were found for methyl acetate solubility in alkane hydrocarbons. However, based on handbook data that show butyl acetate is miscible with benzene, it is expected that methyl acetate would also be miscible with alkanes. See Tables for Identification of Organic Compounds, Charles D. Hodgman, Robert C. Weast and Samuel M. Selby, 1960. p. 222.

Discussion of Alternative Antifreeze Agents

Even if alternative antifreeze agents can be identified, the question follows: what advantage do they have? Why change from the status quo, methanol? Possible reasons could be that the proposed substance:

- is a more effective antifreeze
- is less acidic and therefore less corrosive
- costs less
- provides some other benefit.

Considering these points:

- Methanol is effective to -54 C (-65 F). This is sufficient, so alternative antifreeze agents would not be more effective as an antifreeze.
- Looking at the acidity data, all of the alternatives would be expected to be less acidic than methanol, so it is possible that an alternative antifreeze agent could be less corrosive. However, it is not clear that methanol has a corrosion problem, particularly if the amounts of methanol limited to the amount really needed to prevent freezing.
- Another antifreeze could provide a benefit if it had less tendency to form a second phase. In other words, the antifreeze agent would be a good co-solvent for water and in propane. Ternary solubility data for the propane-water-antifreeze agent system are necessary to make an accurate assessment of co-solvent effectiveness and such data are not available for the candidates. The respective solubilities of the antifreeze agent in water and hydrocarbon can be used as an indicator, since to be a good co-solvent the agent must be compatible with both water and propane. On this score, tetrahydrofuran appears to be worthy of further investigation.
- In terms of cost, methanol is made directly from natural gas in large volumes. Thus, it seems unlikely that any of the other candidates would be less expensive.
- If new antifreeze were to be used, unless the industry would change completely and instantly to the new compound (unlikely), propane with the new antifreeze compound would be supplied together with propane containing methanol. Thus, any new antifreeze would need to be compatible the methanol antifreeze that is already in use.

Recommendations

Overall, it appears that there is no obvious alternative to methanol and little reason to change from methanol as an antifreeze agent.

Knowledge Gaps

For a number of alternative antifreeze agents solubility information is not available for propane-agent or propane-water-agent. Without this information effectiveness, treat rates and temperature limits cannot be fully and accurately predicted.

Conclusions

Understanding of the Technical Basis for Methanol Use

Even though the physical chemistry data for systems containing propane, water, and methanol are not complete, considerable insight into the behavior of methanol as an antifreeze can be obtained. In particular more data are needed on the solubility of methanol in propane and on the degree to which this solubility changes with temperature and with water content. More data are also needed to define the K ratios that describe how the amount of methanol in propane vapor is related to the amount of methanol in the liquid propane.

The development and validation of an equation of state for the propane-water-methanol system would provide a theoretical foundation for describing the complete behavior of this system. Although past equations of state could not handle such highly non-ideal situations, recent (post 2000) advances indicate that developing a reasonably accurate equation of state for propane-water-methanol would now be feasible.

Measurement of Water and Methanol

None of the existing methods for measuring water and methanol are sufficiently accurate, free from interferences and usable in the field. Currently, NDIR-based meters are able to let field technicians monitor ppm levels of other gases, such as carbon dioxide. Using this technique for monitoring the water and methanol content of propane would remove much of the uncertainty associated with limiting water content and managing methanol addition.

Effect of Methanol on Materials

There are some data gaps and uncertainties concerning the action of propane with added methanol on aluminum cylinders, on some elastomers and with regards to stress cracking. However, overall, neither the technical literature nor the long experience with methanol indicates that there are significant materials problems.

Effect on Fuel Vaporization

No significant problems are indicated. The main uncertainty is that data are lacking to clearly define the limiting amounts of water and methanol in propane, and the limiting temperature conditions, beyond which a separate water- or methanol-rich layer will be formed. If liquid from such a layer were vaporized and/or fed to combustion equipment, there would be operational problems.

Alternatives to Methanol

A systematic examination of all chemical compounds with appropriate properties did not identify any alternatives that would be superior to methanol. Moreover, no candidates were identified that would be able to match methanol's combination of effectiveness, relative lack of operational problems, and low cost.

Usage Recommendations

By making some reasonable assumptions about the amount of water that could be dissolved in liquid propane, the relationship of the water and methanol composition of vapor derived from that liquid, and the amount of methanol needed to protect the water in that vapor from freezing, it is possible to estimate the amount of methanol needed. This is about 450 mass ppm of methanol in the liquid propane. Applying a safety factor to account for uncertainty in our knowledge of the physical chemistry, a methanol addition rate of 600 mass ppm is recommended.

This addition rate is equivalent to 4.9 volume ounces of methanol per 100 gallons of propane, or 49 volume ounces (slightly more than 3 pints) per 1000 gallons.

Literature

Because the literature sources on properties related to the propane-water-methanol system are scattered, the following section provides a bibliography of relevant literature citations. In order that to place these citations in context, each listing contains comments and an example of key results. Of course the full reference should be consulted to see the context of any quoted results.

Kuenen, 1903

Reference:

On the Mutual Solubility of Liquids -- II, J.P. Kuenen,, Philosophical Magazine, 6 , 637 (1903).

✓ Experimental	✓ Propane
- Equation of State	- Water
	✓ Methanol
	- Related substance –

Contents:

Presents experimental data on mutual solubility of methanol and propane. It is noticed that two liquid phases are formed, but that as the temperature is increased the two liquid layers become identical. Table III from the paper shows this critical temperature for various pressures.

TABLE III.—Propane and Methyl-alcohol.

Critical points of liquids.

Temp.	Press.	Temp.	Press.
21·15	10	18·6	55
20·85	11	18·05	70
20·8	13	17·85	79
20·05	23	17·8	82
19·85	26	17·65	85
19·4	34·5	17·5	93
19·2	39	17·4	95
19·0	46	17·2	(100)

Comments:

Based on measured critical point data, the propane was reported to be impure. This was before the invention of gas chromatography and it is not certain what impurities were present. No information is given on the amounts (mole fractions) of propane and methanol.

4392

Kretschmer and Wiebe, 1951

Reference:

Solubility of Gaseous Paraffins in Methanol and Isopropyl Alcohol, Carl B. Kretschmer, Richard Wiebe, JACS, 74, 1276 (1952).

✓ Experimental	✓ Propane
- Equation of State	- Water
	✓ Methanol
	- Related substance –

Contents:

As the title states, the paper contains experimental data on the solubility of propane in methanol. Table I from the paper shows the data.

TABLE I

VAPOR PRESSURE OF SOLUTIONS OF HYDROCARBONS IN METHANOL

Solute	Temp., °C.	x_2[a]	p[b]
Propane	0.00	0	30.4
		0.02039	756.4
	25.00	0	126.9
		0.004988	464.0
		.007040	598.1
		.009569	759.6
	50.00	0	416.1
		0.003232	758.4

[a] Mole fraction of hydrocarbon. [b] Total pressure in mm.

Comments:

1.. This paper contains good data on the solubility of propane in methanol, but not data on methanol in propane.

2. The solubilities of methanol in propane are very small, about 1 mole percent at 25 C and 1 atm. This is in contrast to data for hexane in Kotogeorgis, et al., 2000.

4391

Reamer, et al., 1952

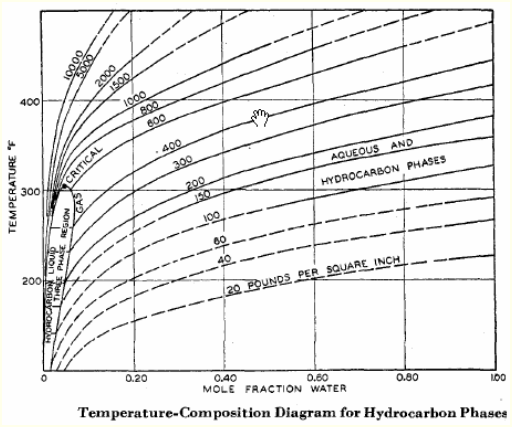
Reference:

Phase Equilibria in Hydrocarbon Systems, H.H. Reamer, B.H. Sage, and W.N. Lacey, Industrial and Engineering Chemistry, 44, 609 (1952).

- ✓ Experimental
- - Equation of State
- - Propane
- ✓ Water
- - Methanol
- ✓ Related substance – n-butane

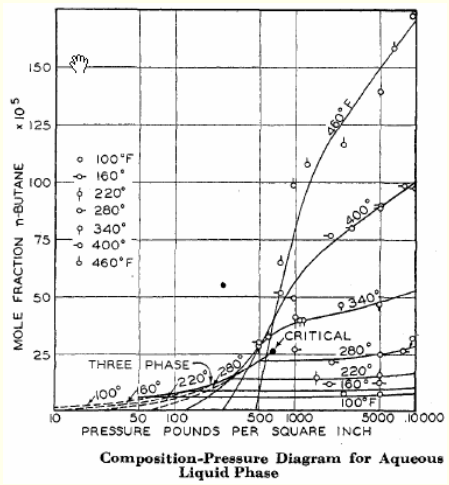
Contents:

Detailed phase diagram data and graphs of n-butane-water system. Temperature and pressures are in common LP gas fuels range. Graph A and B show summary of data.



Temperature-Composition Diagram for Hydrocarbon Phases

Graph A



Composition-Pressure Diagram for Aqueous Liquid Phase

Graph B

Comments:

A good resource, but no data on propane. Other papers by this author cover methane and ethane.

4426

Kobayashi and Katz, 1953

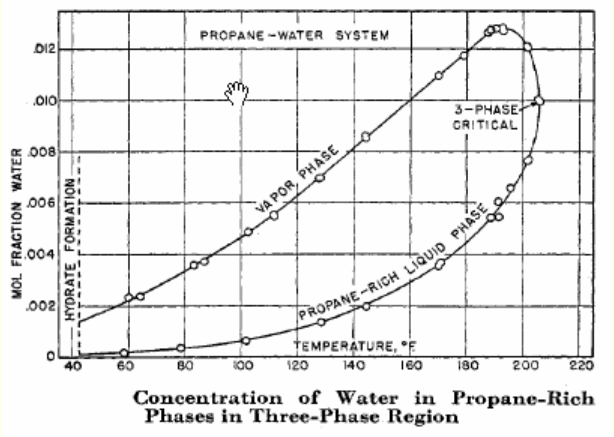
Reference:

Vapor-Liquid Equilibria For Binary Hydrocarbon-Water Systems, Riki Kobayashi, Donald L. Katz, Ind. Eng. Chem., 45, 440 (1953).

✓ Experimental	✓ Propane
- Equation of State	✓ Water
	- Methanol
	- Related substance –

Contents:

Experimental data on propane-water system. Graphs A and B show the concentration of water in propane-rich and water-rich phases at various temperatures from 4 to 100 C.



Concentration of Water in Propane-Rich Phases in Three-Phase Region

Graph A

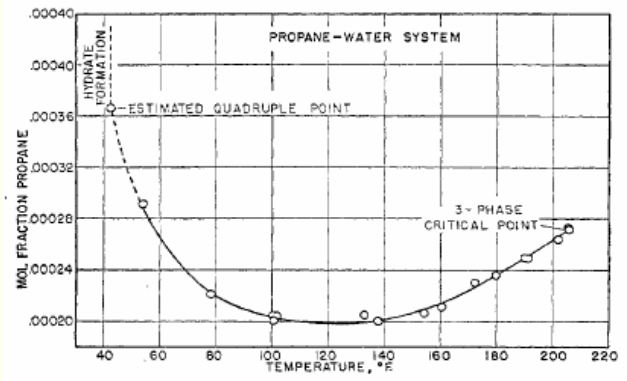


Figure 5. Concentration of Propane in Water-Rich Phase in Three-Phase Region

Graph B

Comments:

Accompanied by extensive data tables on compositions of different phases at different temperatures. An important reference for water solubility data in propane.

4385

Kogan, et al., 1956

Reference:

Solubility in Systems Consisting of Methanol, Water, and Normal Paraffin Hydrocarbons, V.B. Kogan, I.V. Deizenrot, T.A. Kuldyaeva, and V.M. Fridman, J. Applied Chem. USSR, **29**, 1493 (1956).

Contents:

- ✓ Experimental
- ✓ Equation of State
- - Propane
- ✓ Water
- ✓ Methanol
- ✓ Related substance – n hexane to n-nonane

Contents:

Contains detailed phase diagram information for n-hexane, n-heptane, n-octane, and n-nonane. The figure below shows results for these substances.

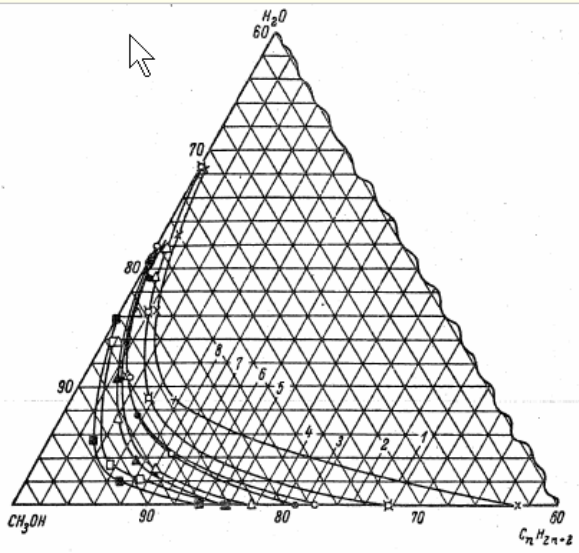


Fig. 2. Mutual solubility in three-component systems methanol–water–hydrocarbon at 10 and 20° (in wt. %).
1) Methanol–water–n-hexane at 20°, 2) methanol–water–n-hexane at 10°, 3) methanol–water–n-heptane at 20°, 4) methanol–water–n-heptane at 10°, 5) methanol–water–n-octane at 20°, 6) methanol–water–n-octane at 10°, 7) methanol–water–n-nonane at 20°, 8) methanol–water–n-nonane at 10°.

Comments:

This paper shows the type of data that are desired for the propane-methanol-water system. Note that for these hydrocarbons, the presence of even a small amount of water greatly reduces the solubility.

4517

Timmermans, 1959	
Reference: Physico-Chemical Constants of Binary Systems in Concentrated Solutions, Jean Timmermans, (1959).	
✓ Experimental	✓ Propane
- Equation of State	- Water
	✓ Methanol
	- Related substance –
Contents: Table of critical solution temperatures for propane methanol.	
Comments: A secondary source that quotes data from Kuenen, 1903. 4377	

Francis, 1961	
Reference: Critical Solution Temperatures, Alfred W. Francis, , Advances in Chemistry Number 31, 155 (1961).	
✓ Experimental	✓ Propane
✓ Equation of State	✓ Water
	✓ Methanol
	✓ Related substance –
Contents: Tables of critical solution temperatures.	
Comments: A secondary source that quotes data from Kuenen, 1903. 4373	

Kiser, et al., 1961

Reference:

Solubilities of Various Hydrocarbons in Methanol, Robert W. Kiser, G. Dana Johnson, and Martin D. Shetlar, J. Chem. Eng. Data, 6, , 338 (1961).

✓ Experimental	- Propane
- Equation of State	- Water
	✓ Methanol
	✓ Related substance – pentane, other n-alkanes

Contents:

Solubility and phase diagram data for n-alkanes from pentane to decane plus some isoalkanes.

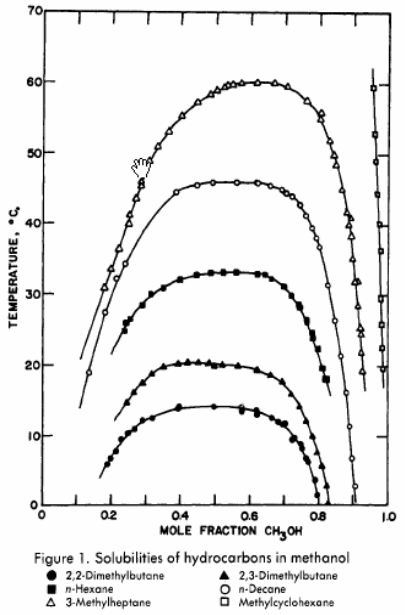


Figure 1. Solubilities of hydrocarbons in methanol

Graph A

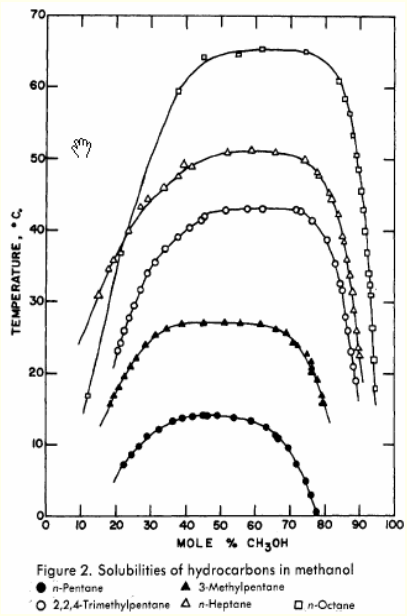


Figure 2. Solubilities of hydrocarbons in methanol

Graph B

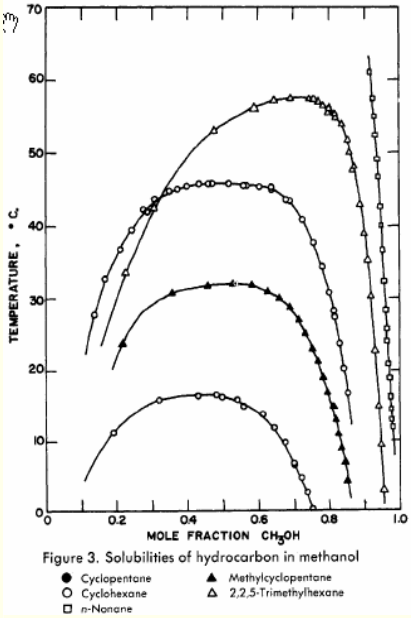


Figure 3. Solubilities of hydrocarbon in methanol

Graph c

Comments:

Data seem somewhat inconsistent in that when looking at the n-alkanes from n-octane down to n-pentane, there is not a consistent increase in solubility.

Solubility of methanol in the smallest n-alkane studied, pentane, is about 26 mole percent at 10 C, leading one to expect that solubility of methanol in propane would be larger.

4425

Ma and Kohn, 1964

Reference:

Multiphase and Volumetric Equilibria of the Ethane-Methanol System at Temperatures between -40 and 100 C, Yi Hua Ma, James P. Kohn, J. Chem. Eng. Data, 9, 3 (1964).

✓ Experimental	- Propane
✓ Equation of State	- Water
	✓ Methanol
	✓ Related substance – ethane

Contents:

This paper notes that Kuenen, observed two liquid phases for mixtures of ethane and methanol, but did not report the composition of the phases and intends to fill that gap.

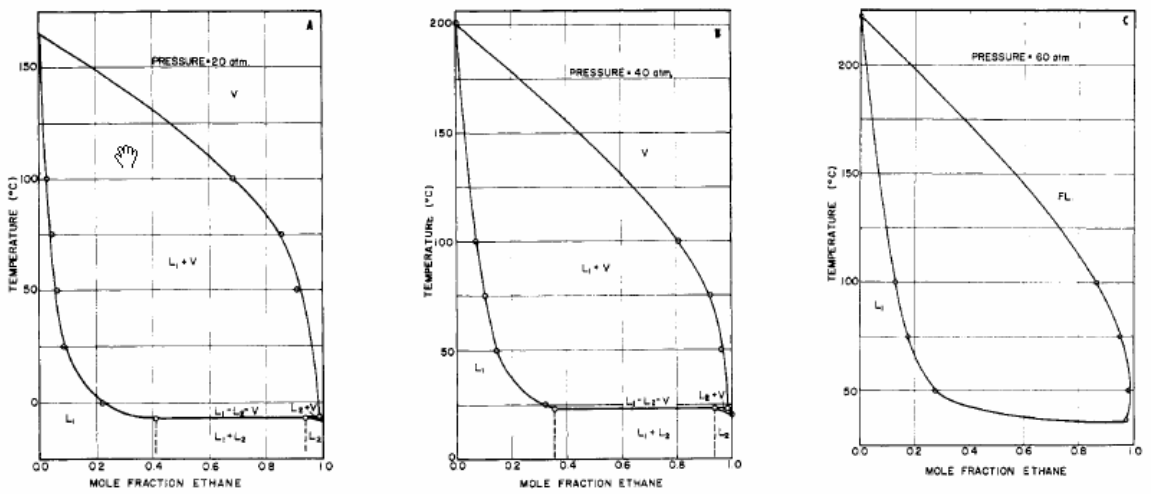


Figure 2. Isobaric temperature–composition diagram
A: 20 atm. pressure, B: 40 atm. pressure, C: 60 atm. pressure

Comments:

The graphs show that for ethane-methanol at 20 atm, at temperatures below about -4 C, there exists two liquid phases: a methanol-rich liquid and a propane-rich liquid and that the propane-rich liquid can contain up to about 10 percent methanol.

4376

Parish and Prausnitz, 1972

Reference:

Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures, William R. Parrish, John M. Prausnitz, Ind. Eng. Chem. Process Des. Develop., 11, 26 (1972).

- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- ✓ Water
- \- Methanol
- \- Related substance –

Contents:

Data on propane hydrates. Able to fit this data with an EOS. Graph A shows key results.

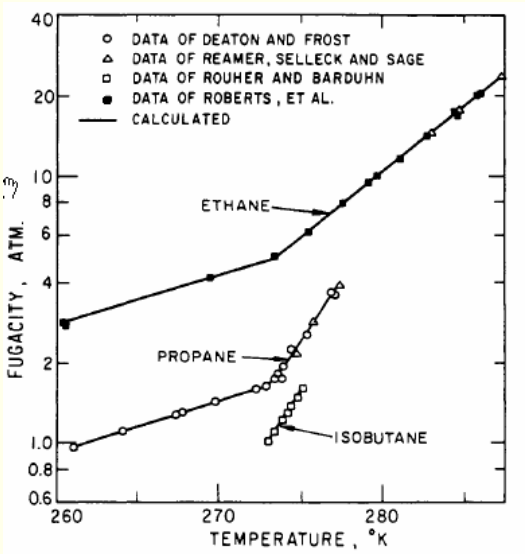


Figure 3. Dissociation fugacities of ethane, propane, and isobutane hydrates

Graph A

Comments:

None.

4361

Noda, et al., 1975

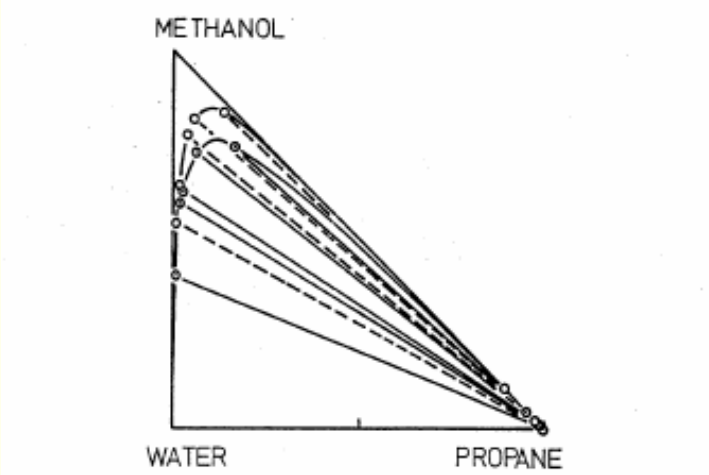
Reference:

Ternary Liquid-Liquid Equilibria for the Systems of Aqueous Methanol Solutions and Propane or n-Butane, Katsuji Noda, Kuraji Sato, Koichi Nagatsuka and Kiyoharu Ishida, J. Chem. Eng. Japan, 8, 492 1975).

✓ Experimental	✓ Propane
- Equation of State	- Water
	✓ Methanol
	✓ Related substance – n-butane

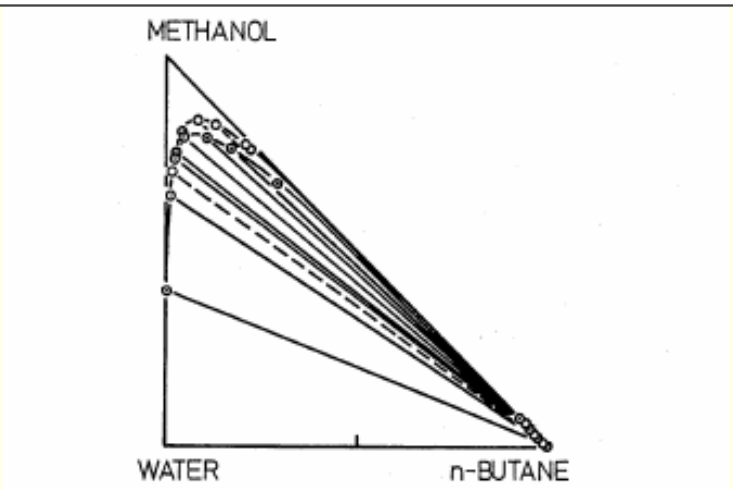
Contents:

Presents experimental data for propane-water-methanol system. Also data for n-butane.



Liquid-liquid equilibria for the methanol-water-propane system at 0°C (○) and 20°C (⊙), weight fraction

Graph A



Liquid-liquid equilibria for the methanol-water-*n*-butane system at 0°C (○) and 20°C (⊙), weight fraction

Graph B

Comments:

Best data source of experimental data on behavior of propane-water-methanol system.

4424

Robinson, et al., 1985

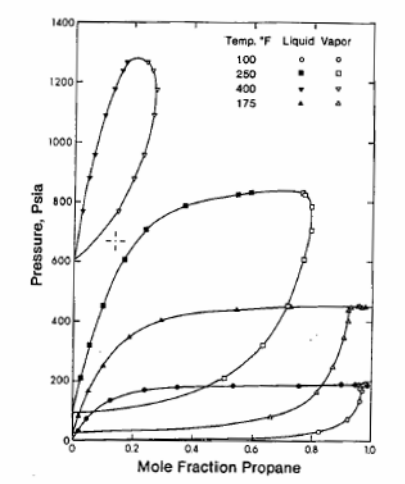
Reference:

Development of the Peng-Robinson Equation and its Application to Phase Equilibrium in a System Containing Methanol, Donald B. Robinson, Ding-Yu Peng and Samuel Y-K Chung, Fluid Phase Equilibria, 24, 25 (1985).

- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- ✓ Water
- ✓ Methanol
- \- Related substance –

Contents:

Describes the application of an EOS to water-methanol and methanol-propane systems, among others. Graph A shows example data for propane-methanol system.



Graph A

Comments:

No calculations or data are presented for temperatures less than 38 C (100 F). Does not describe liquid phase composition. Good potential to calculate needed results, but may be superseded by newer approaches.

4389

Stryjek and Vera, 1986	
Reference: PRSV: An Improved Peng-Robinson Equation of State with New Mixing Rules for Strongly Non-ideal Mixtures, R. Stryjek, J.H. Vera, Canadian J. Chem. Eng., 64, 334 (1986).	
- Experimental ✓ Equation of State	- Propane ✓ Water ✓ Methanol - Related substance –
Contents: Describes EOS calculations for methanol-water system, among others. Presents mixing rules.	
Comments: None. 4405	

Stryjek and Vera, 1986	
Reference: PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures, R. Stryjek, J.H. Vera, Canadian J. Chem. Eng., 64, 323 (1986).	
- Experimental ✓ Equation of State	✓ Propane ✓ Water ✓ Methanol ✓ Related substance–other gases and hydrocarbons
Contents: Describes EOS calculations for mixtures. Provides an extensive list of mixing parameters for a variety of inorganic gases and hydrocarbons, ketones, alcohols, and other organic compounds.	
Comments: None. 4404	

Galivel-Solastiouk, et al., 1986

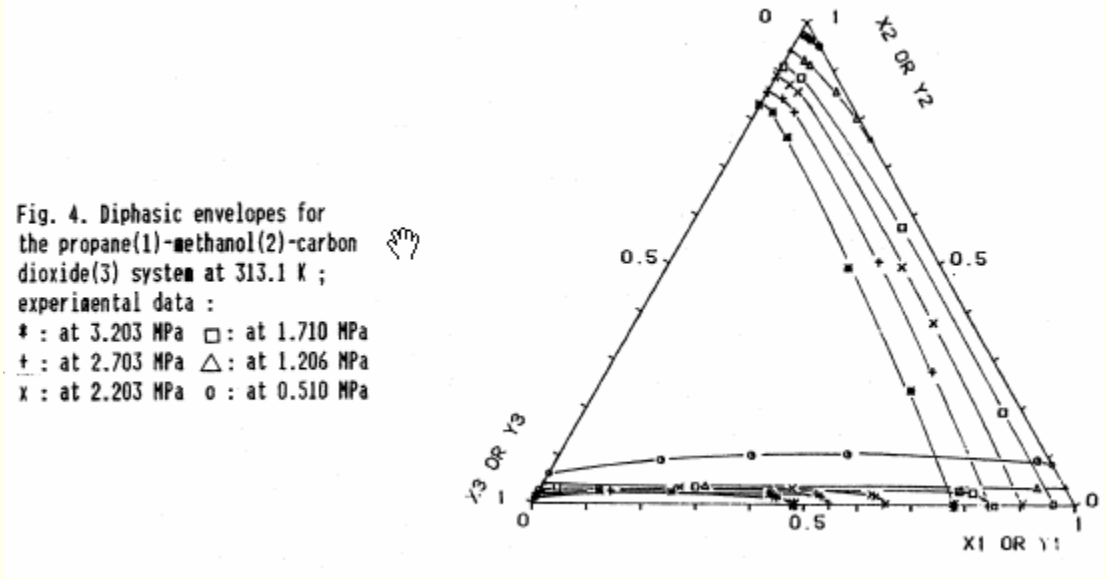
Reference:

Vapor-Liquid Equilibrium Data for the Propane-Methanol and Propane-Methanol-Carbon Dioxide System, Francine Galivel-Solastiouk, Serge Laugier and Dominique Richon, Fluid Phase Equilibria, 28, 73 (1986).

✓ Experimental	✓ Propane
- Equation of State	- Water
	✓ Methanol
	✓ Related substance – carbon dioxide

Contents:

Lists experimental data for the propane-methanol and propane-methanol-carbon dioxide systems. Graph A shows a phase diagram plot of the propane-methanol-carbon dioxide system. In this case carbon dioxide is not of interest and therefore the graph may be read for Xco2 = 0. If this is done



Graph A

Comments:

The temperature is for 40 C. Would really like to have temperatures more in the range of winter propane use. Looking only at the propane-methanol data, the methanol solubility is less than that shown for methanol hexane by Kotogeorgis, et al., 2000. This seems chemically improbable.

4382

Kertes, 1986	
Reference:	
Solubility Data Series	
✓ Experimental	✓ Propane
- Equation of State	✓ Water
	✓ Methanol
	- Related substance –
Contents:	
Solubility data.	
Comments:	
This is a secondary source that quotes Kretschmer and Wiebe, 1951.	
4368	

Schwartzentruber, et al., 1987

Reference:

Representation of the Vapor-Liquid Equilibrium of the Ternary System Carbon Dioxide-Propane-Methanol and its Binaries with a Cubic Equation of State: A New Mixing Rule, Jacques Schwartzentruber, Francine Galivel-Solastiouk and Henri Renon, Fluid Phase Equilibria, 38, 217 (1987).

✓ Experimental	✓ Propane
✓ Equation of State	- Water
	✓ Methanol
	✓ Related substance –

Contents:

Discusses prediction of phase-splitting using cubic EOS. Key results are shown in Graph A.

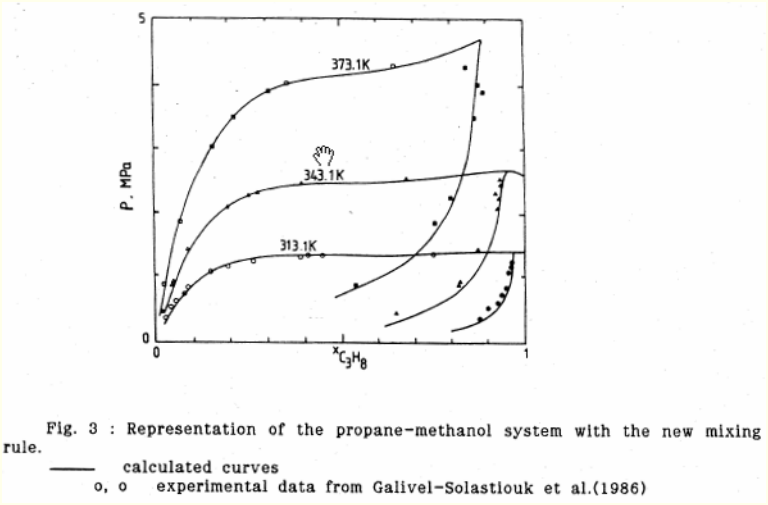


Fig. 3 : Representation of the propane-methanol system with the new mixing rule.
—— calculated curves
o, o experimental data from Galivel-Solastiouk et al.(1986)

Graph A

Comments:

Like other studies, this one does not discuss behavior at temperatures less than 40 C. This is all the more frustrating as the agreement between actual and predicted behavior is very good.

4407

Harmens and Sloan, 1990

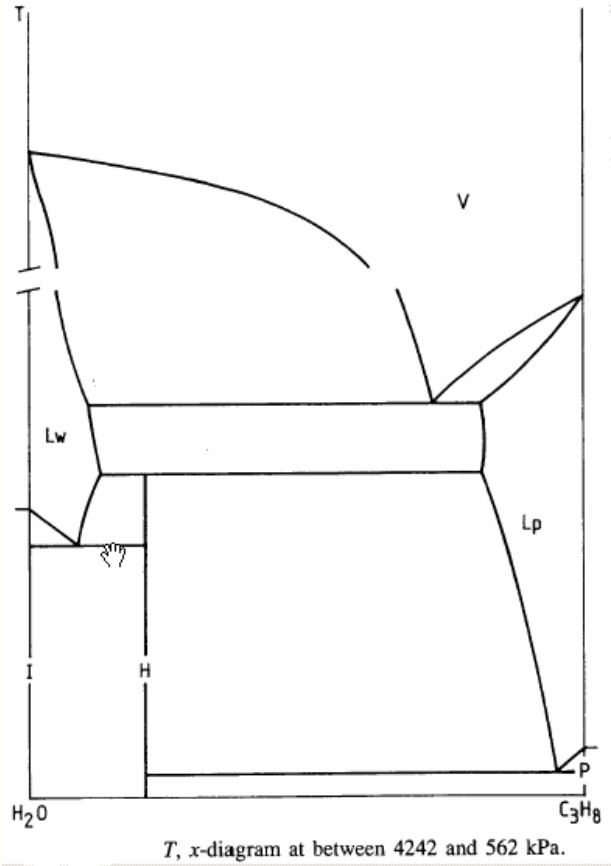
Reference:

Phase Behavior of the Propane-Water System: A Review, A. Harmens, E. Dendy Sloan, Canadian J. Chem. Eng., 68, 151 (1990).

✓ Experimental	✓ Propane
- Equation of State	✓ Water
	- Methanol
	- Related substance –

Contents:

Contains a complete description of the phase behavior of the propane-water system through the entire range of pressures. Includes gas, liquid, solid and hydrate phases.



T, *x*-diagram at between 4242 and 562 kPa.

Graph A

Comments:

The behavior is complex and requires thought and interpretation. The accompanying graphs are only semi-quantitative.

4366

Carroll, et al., 1992

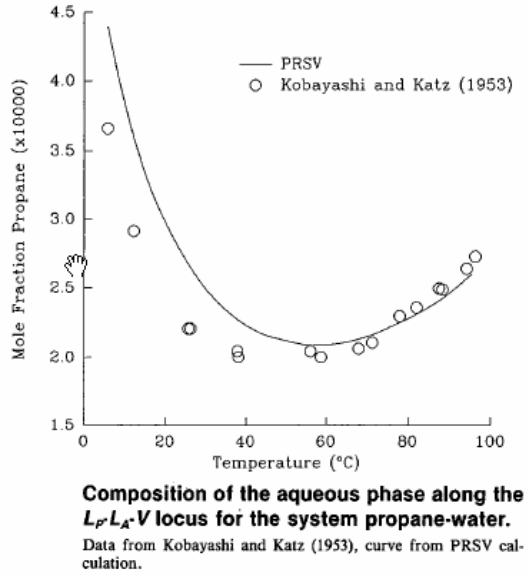
Reference:

Phase Equilibria in the System Water-Methyldiethanolamine-Propane, John J. Carroll, Fang-Yuan Jou, Alan E. Mather, and Frederick D. Otto, AIChE J., 38, , 511 (1992).

- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- ✓ Water
- \- Methanol
- ✓ Related substance –

Contents:

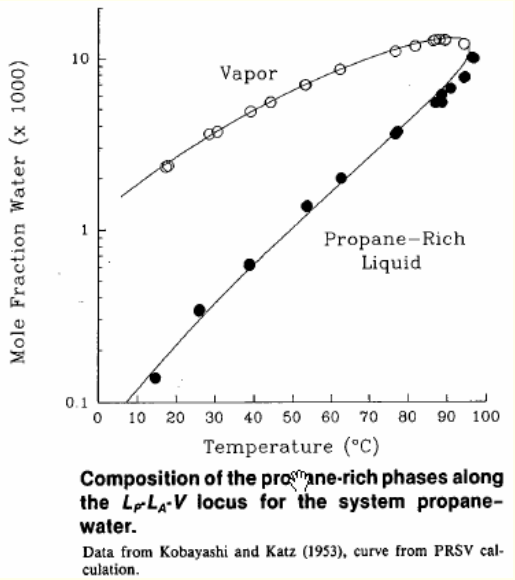
Contains EOS calculations for the propane-water system. Compares to experimental data from the literature.



Composition of the aqueous phase along the L_P-L_A-V locus for the system propane-water.

Data from Kobayashi and Katz (1953), curve from PRSV calculation.

Graph A



Composition of the propane-rich phases along the L_P-L_A-V locus for the system propane-water.

Data from Kobayashi and Katz (1953), curve from PRSV calculation.

Graph B

Comments:

None.

4316

Wong and Sandler, 1992

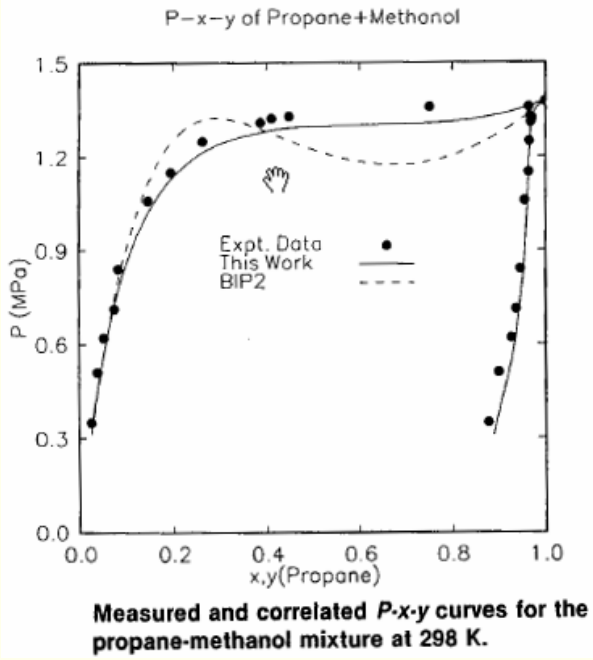
Reference:

Theoretically Correct Mixing Rule for Cubic Equations of State, David Shan Hill Wong, Stanley I. Sandler, AIChE J., 38, 671 (1992).

✓ Experimental	✓ Propane
✓ Equation of State	- Water
	✓ Methanol
	- Related substance –

Contents:

As the title suggests, this paper provides an improved EOS calculation procedure for mixtures.



Measured and correlated *P-x-y* curves for the propane-methanol mixture at 298 K.

Graph A

Comments:

None.

4403

Pedersen, et al., 1996	
Reference: Phase Equilibrium Calculations for Unprocessed Well Streams Containing Hydrate Inhibitors, Karen S. Pedersen, Michael L. Michelsen and Arne O. Fredheim, Fluid Phase Equilibria, 26, 13 (1996).	
- Experimental ✓ Equation of State	- Propane ✓ Water ✓ Methanol ✓ Related substance – hydrocarbons
Contents: Shows the phase distribution of methanol and water between a gas phase, a hydrocarbon liquid phase and an aqueous phase can be represented by the Souve-Redlich-Kwong EOS with additional mixing rules.	
Comments: One of several promising EOS methods. 4364	

Voutsas, et al., 1999

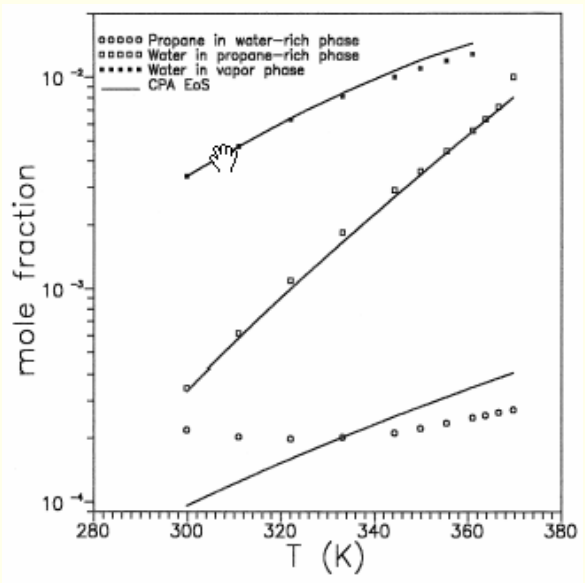
Reference:

Contents:

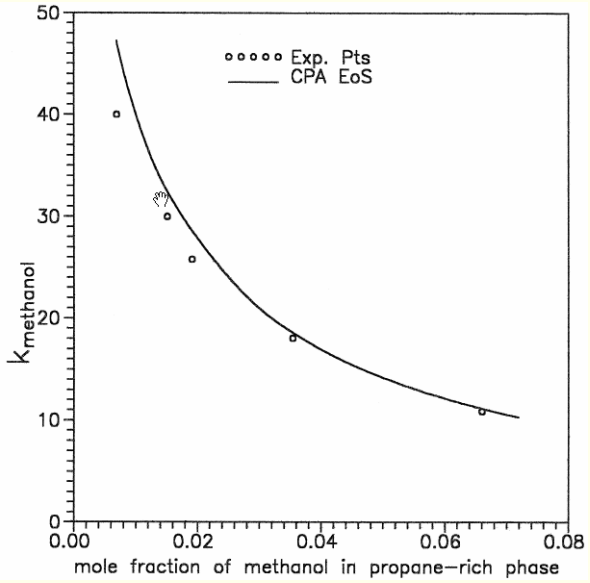
- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- ✓ Water
- ✓ Methanol
- \- Related substance –

Contents:

Describes the use of an equation of state to predict phase equilibria for alkane-water-alcohol systems. For example, Graph A shows solubility of water in propane and propane in water, and Graph B shows partition of methanol between propane-rich and water-rich liquid phases.



Graph A



Graph B

Comments:

Provides specific information on partition ratio of methanol between propane and water layers, but also shows the ability of models to predict such information.

4465

Kontogeorgis, et al., 2000

References:

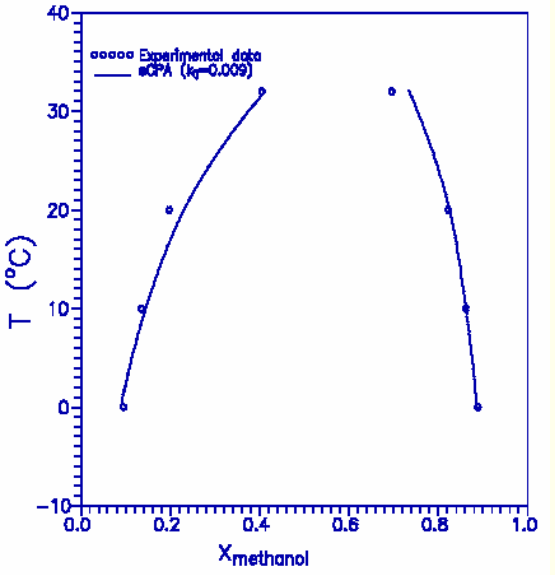
Multicomponent Phase Equilibrium Calculations for Associating Mixtures, Georgios M. Kontogeorgis, Iakovos V. Yakoumis, Henk Meijer, Eric Hendriks and Tony Moorwood, 11 Aug (2000).

Also: Multicomponent Phase Equilibria Calculations for Water-Methanol-Alkane Mixtures, Georgios M. Kontogeorgis, Iakovos V. Yakoumis, Hank Meijer, Eric Hendriks, and Tony Moorwood, Fluid Phase Equilibria, 158, 201 (1999).

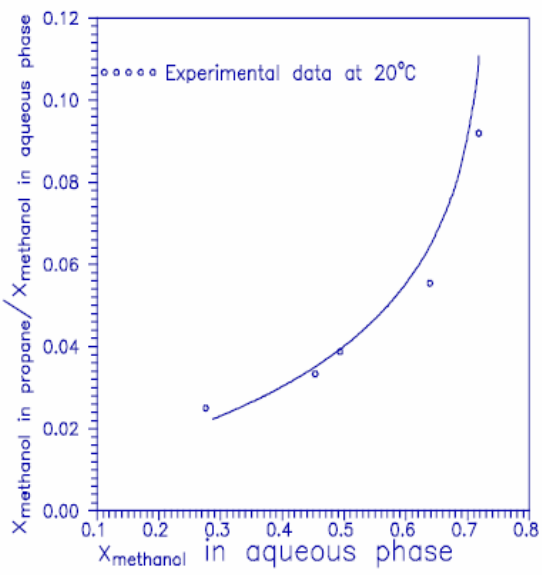
- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- ✓ Water
- ✓ Methanol
- ✓ Related substance – hexane

Contents:

Contains results of sample EOS calculations. Graph A shows methanol solubility in hexane. Based on chemical structure, methanol should be even more soluble in propane. Graph B shows how methanol and water are predicted to distribute.



Graph A



Graph B

Comments:

Methanol solubility in propane would be expected to look like the graph of methanol solubility in hexane, but be more soluble.

4317

Blanco, et al., 2001

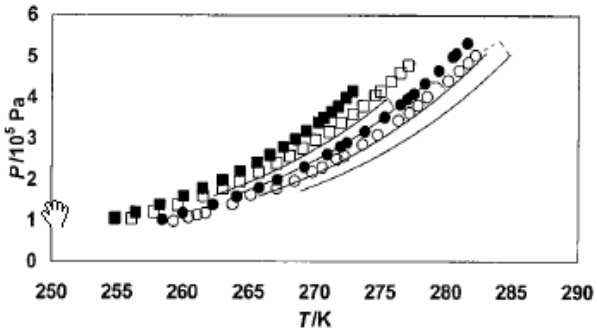
Reference:

Dew Points of Ternary Propane + Water + Methanol: Measurement and Correlation, Sofia Blanco, Immaculada Velasco, Evelyne Rauzy and Santos Otin, J. Chem. Eng. Japan, 34, 971 (2001).

- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- ✓ Water
- ✓ Methanol
- \- Related substance –

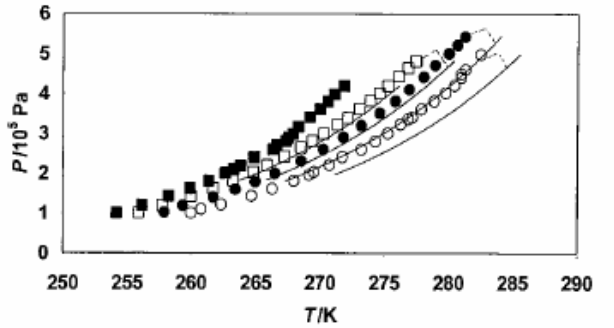
Contents:

Presents experimental data for dew points of propane-water-methanol system and shows correlation with EOS calculations.



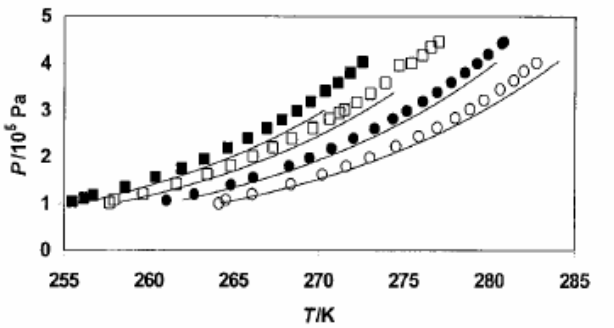
Comparison between experimental dew point curves (symbol) and calculated with the EOS-CR method (line) for the system {$(1 - y_1 - y_2)$ propane + y_1 water + y_2 methanol}: ■, $y_1 = 0.00036$, $y_2 = 0.0088$; □, $y_1 = 0.00052$, $y_2 = 0.0098$; ●, $y_1 = 0.00064$, $y_2 = 0.0108$; ○, $y_1 = 0.00078$, $y_2 = 0.0130$

Graph A



Comparison between experimental dew point curves (symbol) and calculated with the EOS-CR method (line) for the system {(1 − y_1 − y_2) propane + y_1 water + y_2 methanol}: ■, y_1 = 0.00055, y_2 = 0.0081; □, y_1 = 0.00074, y_2 = 0.0084; ●, y_1 = 0.00091, y_2 = 0.0096; ○, y_1 = 0.00117, y_2 = 0.0102

Graph B



Comparison between experimental dew point curves (symbol) and calculated with the EOS-CR method (line) for the system {(1 − y_1 − y_2) propane + y_1 water + y_2 methanol}: ■, y_1 = 0.00107, y_2 = 0.0041; □, y_1 = 0.00133, y_2 = 0.0046; ●, y_1 = 0.00186, y_2 = 0.0046; ○, y_1 = 0.00249, y_2 = 0.0049

Graph C

Comments:

Contains experiment data that is useful for comparison with model results.

4315

Li and Englezos, 2003

Reference:

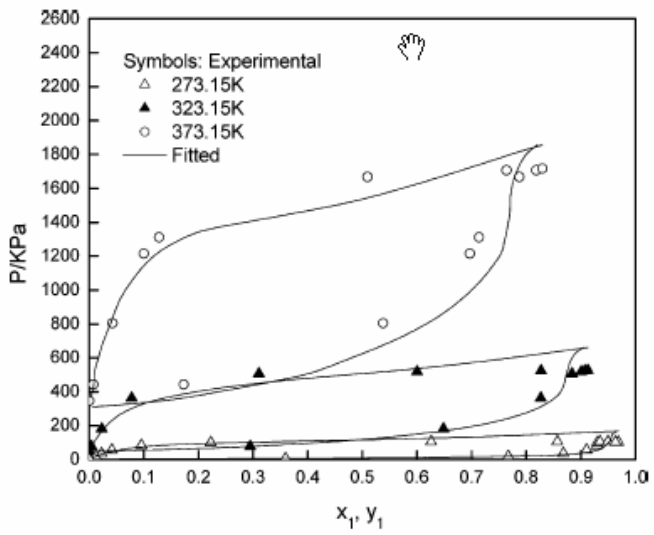
Vapor-Liquid Equilibrium of Systems Containing Alcohols Using the Statistical Associating Fluid Theory Equation of State, Xiao-Sen Li, Peter Englezos, Ind. Eng. Chem. Res., 42, 4953 (2003).

- Experimental
- ✓ Equation of State

- Propane
- ✓ Water
- ✓ Methanol
- ✓ Related substance – butane

Contents:

Describes EOS calculations hydrocarbon-alcohol systems. Graph A compares results to experimental data.



Calculated results of vapor–liquid equilibrium for the butane (1)/methanol (2) system at 273.15, 323.15, and 373.15 K.

Graph A

Comments:

None.

4370

Lee, 2003

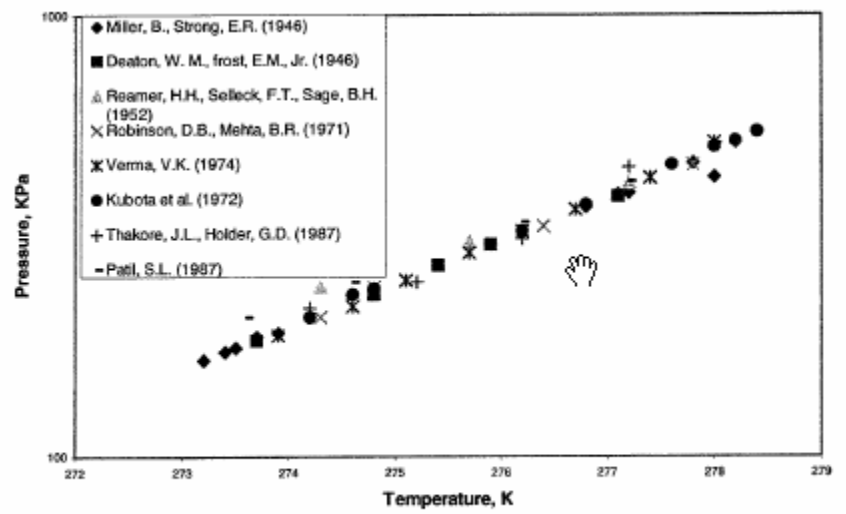
Reference:

Phase Equilibria in Systems Containing Hydrocarbon, Water, and Methanol, Jae Hyuk Lee, , M.S. Thesis, University of Texas at Austin, May (2003).

✓ Experimental	✓ Propane
- Equation of State	✓ Water
	✓ Methanol
	✓ Related substance – ethane, butane

Contents:

Reviews experimental data on propane-water and propane hydrates (See Graph A).



H- L_w -V Phase Data for Simple Hydrates of Propane

Graph A

Comments:

Good review of literature, but no new experimental data or calculated results.

4416

Joung, et al., 2004

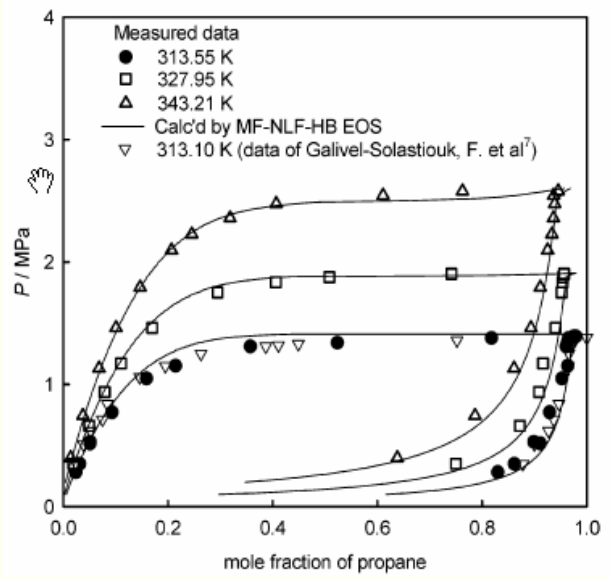
Reference:

High-Pressure Vapor-Liquid Equilibrium Data and Modeling of Propane + Methanol and Propane + Ethanol Systems, Sueng Nam Joung, Hun Yong Shin, Han Seok Kim and Ki-Pung Yoo, J. Chem. Eng. Data, 49, 426 (2004).

- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- ✓ Water
- ✓ Methanol
- ✓ Related substance – hexane

Contents:

Shows experimental data for propane-methanol system. Graph A shows these data. Note that they show only one liquid phase for all the temperatures listed.



Graph A

Comments:

Temperatures range from 40 C to 70 C, which is above the range of interest for winter propane use.

4387

Li and Englezos, 2004

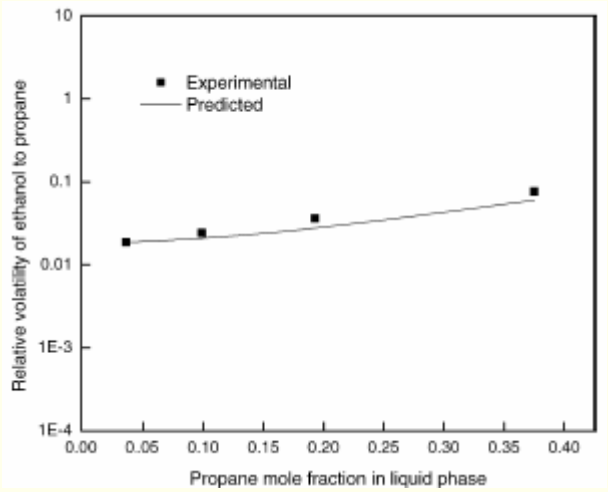
Reference:

Vapor-Liquid Equilibrium of Systems Containing Alcohols, Water, Carbon Dioxide and Hydrocarbons Using SAFT, Xiao-Sen Li, Peter Englezos, Fluid Phase Equilibria, 224, 111 (2004).

- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- ✓ Water
- ✓ Methanol
- ✓ Related substance – butane, ethane

Contents:

Describes EOS calculations using SAFT. Has a complete table of binary interaction coefficients for 18 combinations of hydrocarbons and alcohols.



Graph A

Comments:

Agreement between model results and experimental data appears very good for the propane-water-ethanol system, even for liquid phase compositions. Seems like a promising method to apply to propane-water-methanol. For example, Graph A shows relative volatilities of ethanol and propane as a function of propane mole fraction. Such data are needed for methanol and propane.

4369

Yarrison and Chapman, 2004

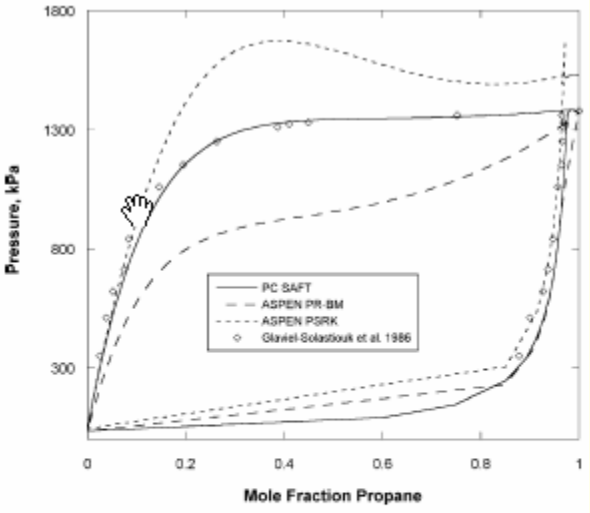
Reference:

Systematic Study of Methanol + n-Alkane Vapor-Liquid and Liquid-Liquid Equilibria Using the CK-SAFT and PC-SAFT Equations of State, Matt Yarrison, Walter G. Chapman, Fluid Phase Equilibria, 226, 195 (2004).

- ✓ Experimental
- ✓ Equation of State
- ✓ Propane
- \- Water
- ✓ Methanol
- ✓ Related substance – other n-alkanes

Contents:

A comparison of EOS methods for predicting alkane-methanol properties, including propane-methanol.



VLE with the methanol + propane system at 313 K [25]. Dashed lines are the ASPEN suggested k_{ij} parameters for the Peng–Robinson Boston–Mathias (PR–BM) equation of state. PC-SAFT correctly shows the presence of an azeotrope, while the PR–BM predicts only ideal solution behavior. The predictive Soave–Redlich–Kwong equation of state also poorly correlates the experimental data, and produces liquid–liquid phase splitting. PSRK uses UNIFAC to determine the mixing energy change for unlike molecules.

Graph A

Comments:

Shows both progress in ability to model this system and limitations, even in the ability to predict vapor pressures of pure methanol.

4428

Ruffine, et al., 2005

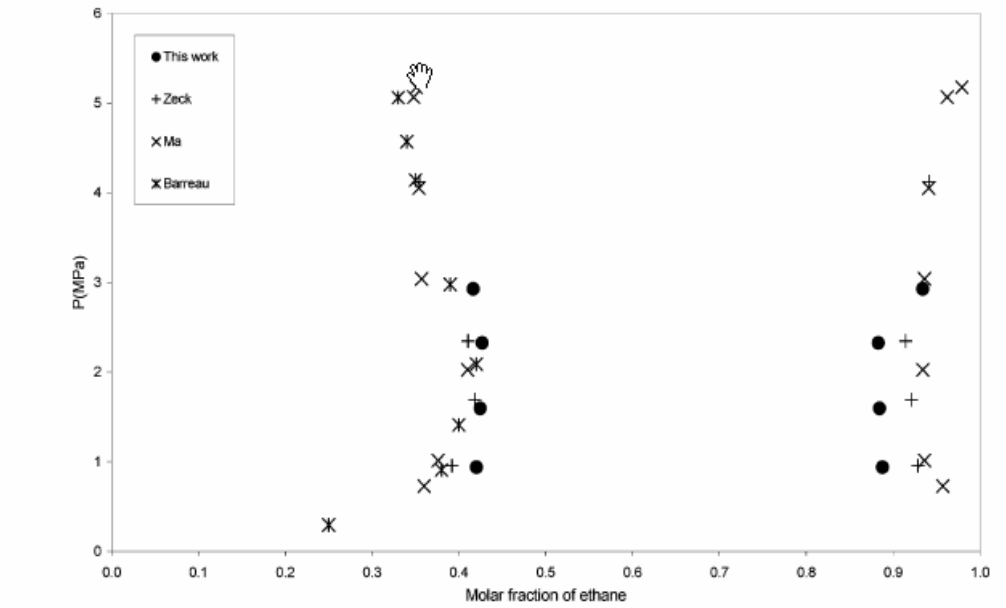
Reference:

New Apparatus for Low-Temperature Investigations: Measurements of the Multiphase Equilibrium of Mixtures Containing Methane, Ethane, Propane, Butane, Methanol, and Carbon Dioxide, L. Ruffine, A. Barreau, I. Brunella, P. Mougin and J. Jose, Ind. Eng. Chem. Res., 44, 8387 (2005).

✓ Experimental	- Propane
- Equation of State	- Water
	✓ Methanol
	✓ Related substance – ethane

Contents:

Describes the apparatus and gives experimental measurements. Compared data to previous investigators.



Three-phase equilibrium for the ethane–methanol system: liquid phase compositions.

Graph A

Comments:

Although clearly ethane is not propane, nonetheless this paper has information that suggests how small alkanes behave in terms of phase diagrams.

4390

Folas, 2005

Reference:

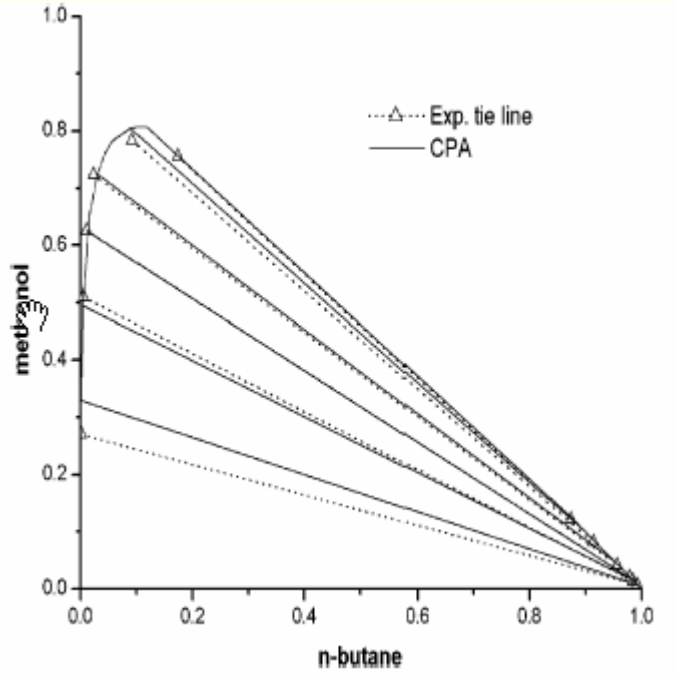
Application of the Cubic-Plus-Association (CPA) Equation of State to Cross-Associating Systems, Georgios K. Folas, Jostein Gabriessen, Michael L. Michelsen, Erling H. Stenby and Georgios M. Kontogeorgis, Ind. Eng. Chem. Res., 44, 3823 (2005).

Contents:

- ✓ Experimental
- ✓ Equation of State
- \- Propane
- ✓ Water
- ✓ Methanol
- ✓ Related substance – butane

Contents:

Describes the cubic plus association model and provides calculated results compared to experimental data. Graph A shows results and data for the n-butane-water-methanol ternary system at 20 C.



Graph A

Comments:

This paper illustrates a very promising model for describing the propane-water-methanol system.

4463

Bruinsma, et al. 2005	
Reference: Novel Experimental Technique for Measuring Methanol Partitioning Between Aqueous and Hydrocarbon Phases at Pressures Up to 69 Mpa, D.F.M. Bruinsma, J.T. Desens, P.K. Notz, and E.D. Sloan, Fluid Phase Equil., 222, 311 (2004). Methanol Solubility in Hydrocarbon Fluids with Liquid Structure Determinations Using Kirkwood-Buff Theory of Mixtures, Douwe Bruinsma, Ph.D. thesis, Colorado School of Mines, (2005).	
Contents:	
✓ Experimental ✓ Equation of State	- Propane ✓ Water ✓ Methanol ✓ Related substance – heptane
Contents: This work describes an experimental technique that can provide K ratios for methanol in hydrocarbons. Most work was done with methanol plus decane and benzene.	
Comments: This technique certainly appears to be applicable to the propane-methanol-water system. The thesis contains an appendix with a list of literature data sources for methanol-hydrocarbon data. The list does not contain any references to sources for methanol-propane data. 4514,4515	

Gil, et al., 2006	
Reference: Dew Points of Binary Propane or n-Butane + Carbon Dioxide, Ternary Propane or n-Butane + Carbon Dioxide + Water, and Quaternary Propane or n-Butane + Carbon Dioxide + Water + Methanol Mixtures: Measurement and Modeling, L. Gil, S. Avila, P. Garcia-Gimenez, S.T. Blanco, C. Berro, S. Otin, and I. Velasco, Ind. Eng. Chem. Res., 45, 3974 (2006).	
✓ Experimental ✓ Equation of State	✓ Propane ✓ Water ✓ Methanol ✓ Related substance – Carbon dioxide
Contents: Contains experimental data for dew points of mixtures of methanol, water, and a gas mixture containing mostly carbon dioxide with some propane or butane.	
Graph A	Graph B
Comments: The procedure presented for calculation of dew points produces calculated vapor pressures that are within about 20 percent of measured values. The same procedure should be able to provide dew points for the propane-water-water system. 4446	

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"Application of the Cubic-Plus-Association (CPA) Equation of State to Cross-Associating Systems," Georgios K. Folas, Jostein Gabriessen, Michael L. Michelsen, Erling H. Stenby and Georgios M. Kontogeorgis, *Ind. Eng. Chem. Res.*, 44, 3823 (2005).

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