Experimental Study of the Phase Equilibria for CO_2 in Liquified Natural Gas Components at 77-219K

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ABSTRACT: In order to prevent roll-over and a rapid boil-off of LNG in tanks, the phase equilibria of carbon dioxide in liquefied natural gas components as binary mixtures at cryogenic temperatures have been experimentally measured using Fourier transform infrared spectroscopy in conjunction with a specially designed variable pressure/temperature cryostat cell (pathlength 2 mm; pressures up to 30 bar). Solid carbon dioxide has been found to be comparatively soluble in liquid nitrogen (3.25×10^{-6} mole fraction), liquid methane (1.04×10^{-4} mole fraction), liquid ethane (3.1×10^{-2} mole fraction) and liquid propane (6.11×10^{-2} mole fraction) at their normal boiling temperatures. The solubilities of carbon dioxide in various cryogens, which increased with increasing temperature, are much lower than those obtained by others using gas chromatography. The differences are attributed to infrared spectroscopy selectively measuring dissolved solute *in situ* whereas gas chromatography measures microscopic particulate solid in addition to dissolved solute.

Nomenclature

T : absolute temperature [K]
S : solubility [mole fraction]

1. Introduction

Liquified natural gas (LNG), i.e. the liquid obtained by condensing gases from subterranean reservoirs, consists largely of methane together with smaller quantities of light hydrocarbons and varying amounts of water, carbon dioxide, nitrogen and other non-hydrocarbon substances. The presence of high-melting impurities, such as carbon dioxide, causes problems in natural gas liquefaction because these impurities can precipitate as solids and block orifices in the process equipment, e.g. submerged pumps and sampling devices. Also during the storage of large amounts of LNG in tanks, typically containing 150,000 m^3, the presence of impurities may affect the convection currents in the LNG and lead to significant effects on boil-off rates. Composition and temperature differences of the LNG components in different layers can lead to "roll-over" and a rapid boil-off, which, given the flammable nature of LNG, may result in serious safety hazards.[1,2]

When handling LNG, therefore, the phase equilibrium properties, e.g. solubility of high melting components in LNG components, needs to be properly determined by reliable experimental studies, so as to ensure the safe operation of plant and equipment. The technique which is widely used in the LNG industry to obtain phase equilibrium data is gas chromatography. This method analyses the composition

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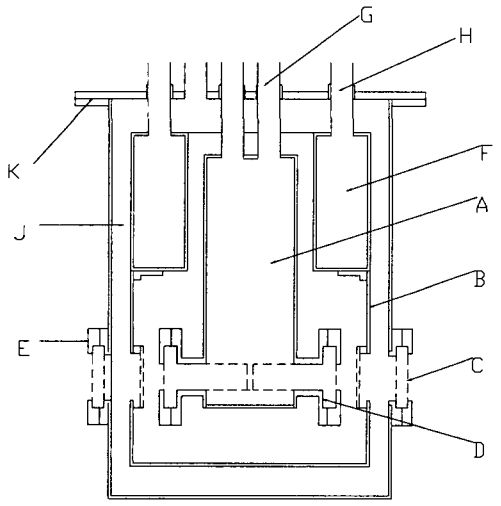
of vapourised gas mixtures.

In this paper the design of a high pressure of 30 bar infrared transmission cryostat and its use to measure the *in situ* solubility of carbon dioxide in various components of LNG are described. The experimental results of the solubilities are presented as a function of temperature for four binary systems, e.g. solid carbon dioxide in liquid nitrogen, liquid methane, liquid ethane and liquid propane.

2. Experiment

A schematic diagram of the high pressure cryostat cell is shown in Fig. 1. The sample chamber (A) is 3.0 cm in diameter and 18.0 cm long and is made of stainless steel (Type 316). This has a bursting pressure of 180 bar enabling the cryostat cell to have a working pressure of 30 bar with a safety factor of 6. The cryostat cell has three optical windows: in the outer wall of the vacuum jacket which is at room temperature; in the liquid nitrogen cooled radiation shield (B) which does not need to be vacuum tight; in the sample chamber which holds the cryogenic liquid sample under investigation. Calcium fluoride discs (C) were used as the optical windows. The outer discs were sealed with 1 mm thick indium wire to the main body of cryostat. A polytetrafluoro ethylene (PTFE) spacer was inserted between the stainless steel cap (E) and the outer side of the window. The indium wire gasket and the PTFE spacer not only achieved sealing, but the PTFE spacer served to relieve any local stresses.



(A) Sample chamber (B) Radiation shield
(C, D) Calcium fluoride discs (E) SUS cap
(F) Nitrogen cooling chamber (G, H) SUS tube
(J) Vacuum chamber (K) 'O' ring

Fig. 1 Schematic diagram of infrared cryostat cell.

The sample chamber (A) and the liquid nitrogen cooling chamber (F) were connected to the top-plate by stainless steel tubes (G, H). The outer vacuum chamber (J) was sealed at the top-plate by a rubber 'O' ring (K). The cooling chamber was mounted with a thin polished copper radiation shield (B) which maintained a constant temperature environment for the sample chamber.

T-shaped brass fittings with CaF_2 windows were used to achieve the desired pathlength of 2.0 mm. The windows were sealed with 1.0 mm diameter indium metal wire and tightened using eight brass screws. The diameter of the window part of the brass tube was 7 mm, which was sufficient for the infrared beam of a Nicolet 7199 Fourier transform infrared spectrometer (beam diameter=3 mm) to pass through. The optical system contained a Michelson interferometer, which has the capability of preserving both the frequency and intensity information during scanning. The resolution used to measure the peak intensities in this research was 1 cm^{-1}.

Before any measurement is started, the cryostat was purged with dry nitrogen gas and the vacuum chamber was evacuated and maintained at a high vacuum of about 10^{-6} torr. A background spectrum was scanned to record any CO_2 or water vapour in the system. This

spectrum served as reference in order to subtract any impurity peaks inthe background spectrum away from the sample spectrum under investigation.

The liquefied sample was prepared in a stainless steel liquefier by exchanging heat with liquid nitrogen and was transferred to the precooled sample chamber of cryostat. After solid carbon dioxide was introduced into the solvent with continuous stirring, a series of spectra were taken at intervals of 2.5 K by about 20 to 40 min stirring, until the carbon dioxide absorption peaks reached the maximum intensity which the F.t.i.r. spectrometer allowed 2.0 absorption unit. The temperature of the solution was directly measured by a Constantan-copper thermocouple which was placed inside the sample chamber. The vapour pressure of the sample was measured using a Bourdon pressure gauge. The temperature and pressure of the solution could be increased by continuous stirring. The saturation condition was achieved by leaving the solution for several minutes without stirring before an infrared scan.

3. Results and discussion

3.1 Phase equilibrium of CO_2 in liquid nitrogen

Infrared spectra for dissolved carbon dioxide in liquid nitrogen are shown in Fig. 2. In the Figure the fundamental band of carbon dioxide at 2349.3 cm^{-1} is overlapped by an induced band of liquid nitrogen at 2345.7 cm^{-1}. The two combination bands at 3605.3 cm^{-1} and 3708.2 cm^{-1} were, therefore, employed for the solubility measurements using the integration of peak area method.[3] The intensities of the two combination bands increased as the temperature increased shown in Fig. 2.

The phase equilibrium, i.e., solubility of carbon dioxide in liquid nitrogen was measured from 78.5 K to near the critical point of liquid nitrogen (119 K) and gave solubilities ranging from 3.25×10^{-6} to 1.98×10^{-4} mole fraction of carbon dioxide in Fig. 3. The data covers a wider temperature range than obtained previously. Interestingly, the solubility values plotted as a semi-log graph as a function of temperature were found to fall almost on a straight line.

The experimental value at 78.5 K is in good agreement with that of Fedorova,[4] but is slight-

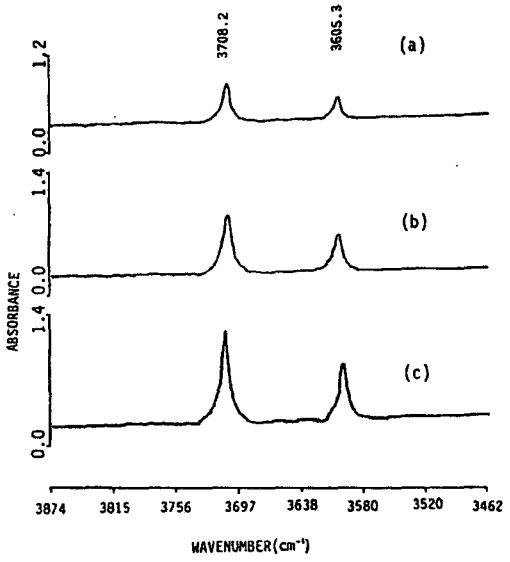


Fig. 2 Infrared spectra of CO_2 in liquid nitrogen: (a) at 98.9 K, (b) at 108.2 K, (3) at 119.1 K.

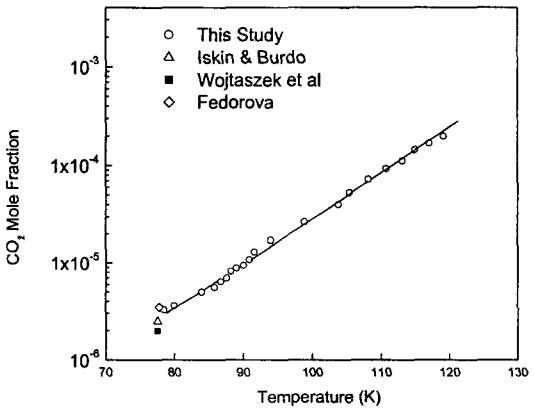


Fig. 3 Solubility of carbon dioxide in liquid nitrogen as a function of temperature.

ly higher than some other measurements.[5,6]

The solubility of carbon dioxide in liquid nitrogen as a function of temperature can be simply expressed as below:

$$\ln S_{CO_2/N_2} = 0.10649T - 20.9938 \quad (1)$$

3.2 Phase equilibrium of CO_2 in liquid methane

Fig. 4 shows a spectrum of carbon dioxide in liquid methane at 139.0 K. The bands due to dissolved carbon dioxide bands at 2349.4, 3598 and 3700.4 cm^{-1} lie between the main peaks of methane and are clearly distinguishable. In order to determine the solubility, the two combination bands at 3598.0 and 3700.4 cm^{-1} were used. Figure shows that the intensity of these two combination bands of carbon dioxide increases as the temperature rises and a strong peak marked as * is due to an overtone band of liquid methane.

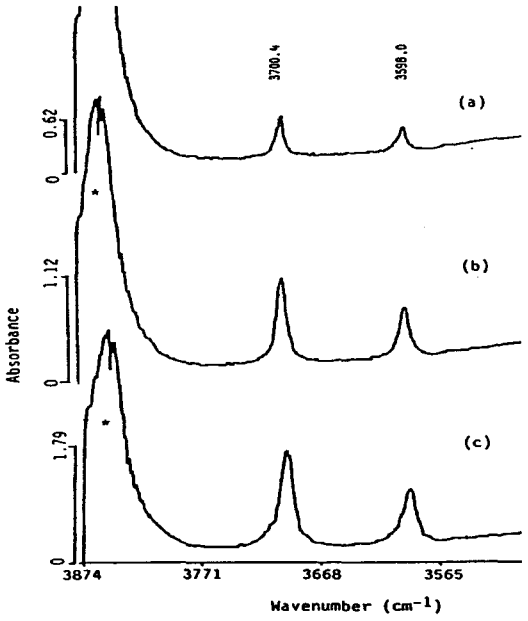


Fig. 4 Infrared spectrum of CO_2 in liquid methane at 123.7 K (The bands marked * exceeded the 2.0 absorbance cut-off of the spectrometer).

Fig. 5 shows the solubility of solid carbon dioxide as a function of temperature in liquid methane as a semi-log graph. The solubility showed values ranging from 1.04×10^{-4} to 8.72×10^{-3} mole fraction of carbon dioxide at 112 K and 170 K, which are much lower than other data obtained using gas chromatography.[7,8]

The solubility of carbon dioxide in liquid methane as a function of temperature can be expressed as below:

$$\ln S_{CO_2/CH_4} = 3.28116\times10^{-4}T^2 - 13.2206 \quad (2)$$

3.3 Phase equilibrium of CO_2 in liquid ethane

The carbon dioxide bands in liquid ethane which are very intense have the same trend as the previous components. The band at 3600 cm^{-1} was used to estimate the solubility because the bands at 3700 cm^{-1} was near to the absorbance limit of the spectrometer.

The semi-log graph in Fig. 6 shows that the measured solubility of carbon dioxide in liquid ethane is very high solubility for carbon dioxide from 3.1×10^{-2} to 8.0×10^{-2} mole fraction at 175 K to 185 K. The values are, however, considerably smaller than the solubility values of

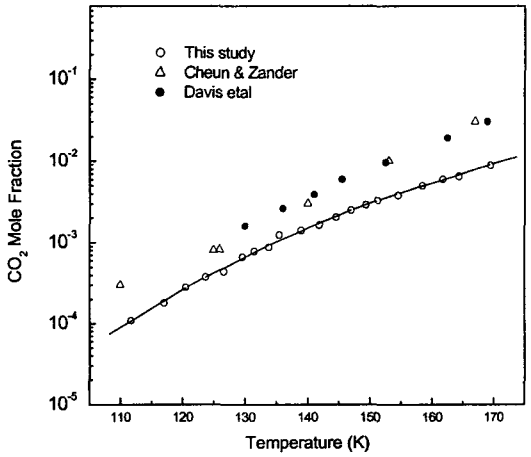


Fig. 5 Semi-log plot of the solubility of carbon dioxide in liquid methane as a function of temperature.

Cheung and Zander[7] and Jensen and Kurata.[9] Above 185 K, the solubility values apparently did not increase, but this was because the tops of the bands were cut off (absorbance > 2.0) due to the strong intensities of solute bands.

3.4 Phase equilibrium of CO_2 in liquid propane

The solute bands of liquid propane at 214.8 K are shown at about 3600 and 3700 cm^{-1}. The peak intensities are extremely strong and partly overlapped. This made it difficult to estimate the solubility of carbon dioxide. When the solid carbon dioxide was introduced in liquid propane at the normal boiling temperature (231.1 K), the temperature of the mixture reduced to 214.8 K due to the endothermic mixing.

Fig. 7 shows the solubility values of carbon dioxide in liquid propane at 214.8 K of 6.11×10^{-2} mole fraction. It was not possible to measure the solubility over as wide a range as for the other cryogens because of the intensities of the solute bands.

4. Discussion

The semi-log plots of solubility as a function of temperature showed approximate linearity over the lower solubility range and deviations at higher solubilities. This reflects the fact that at higher temperatures the peaks approached the absorbance limit of the spectrometer and thus became less reliable.

The linearity at low temperatures can be taken to indicate a lack of interaction effects between the solute and the solvent.

The carbon dioxide in a solution is present as dissolved molecules and particulate solid, which might not be visible to the naked eye. The gas chromatographic technique, which involves evaporating off *all* the solute/solvent measures just the *dissolved* carbon dioxide sample and measuring the amount of carbon dioxide present, measures the both components. The infrared technique, however, because the sharp peaks correspond to the molecular species and the particulate solid gives rise to a very broad multimer envelope. It is not surprising, therefore, that there are differences in values.

5. Conclusion

The experimental results for the binary equilibrium system of carbon dioxide in cryogenic

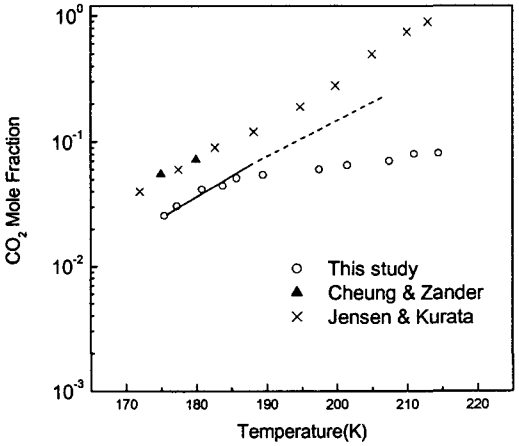


Fig. 6 Semi-log plot of the solubility of carbon dioxide in liquid ethane as a function of temperature.

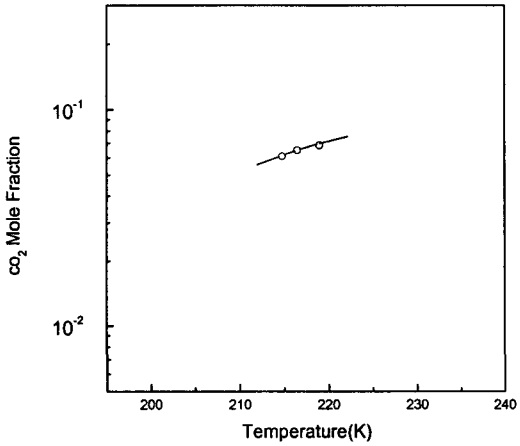


Fig. 7 Semi-log plot of the solubility of carbon dioxide in liquid propane as a function of temperature.

liquids measured by infrared spectroscopy suggest that it can be highly reliable method to measure dissolved solute *in situ* whereas gas chromatography measures microscopic particulate solid in addition to dissolved solute. Data from gas chromatographic studies may have previously overestimated the solubilities of partially soluble solids and that more effort should be to devise *in situ* sampling methods.

Acknowledgement

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