

‘CO₂CKTAILS IN A PIPELINE’: THE PHASE BEHAVIOUR OF CO₂ WITH >20 IMPURITIES

Eduardo Luna-Ortiz¹*

¹ Pace Flow Assurance, London, UK

* Corresponding author e-mail: eduardo@paceflowassurance.co.uk

Abstract

CO₂ in transportation pipelines will contain several impurities due to the wide range of potential emitters. Depending on the physical and chemical nature of the impurities, these will induce diverse phase equilibria. This will be the case even if the impurities are at the ppm level. Certain impurities can induce undesirable liquid phases when the system operates in low pressure single gas phase mode. These liquid phases can appear at normal operating temperatures and can lead to corrosion mechanisms. Thus, there is a need to accurately predict the thermodynamic behaviour of the multicomponent mixture that will be transported in a CCS network. In this work, we investigate the phase behaviour of a CO₂ multicomponent mixture. While the aim is to qualitatively identify the potential number of phases that could form, we focus on the potential issue of liquid dropout at low pressure conditions during gas phase operation.

Keywords: Phase behaviour, Thermodynamics, EoS, CPA, CO₂ transport, Impurities

1. Introduction

Rarely, anthropogenic CO₂ to be transported for geological storage is 100% pure. In most cases, exported CO₂ from capture sites will contain a number of impurities (often at the ppm level but as high as 5% mol of non-condensable gases). This is not only beneficial to the project economics [1] but also reduces energy penalties and associated emissions due to further purification.

Several CO₂ specifications have been developed over the years. In [2], a review of various specifications can be found. The development of these specifications takes into consideration health and safety regulations, industry standards, country legislations and the integrity/flow assurance of the full-chain. Although these specifications serve as guidance and provide a common basis for the design of the components of the CCS system, each project/development will develop its own specification that is appropriate for its own characteristics. Nonetheless, we argue that the limit of impurities should be set, primarily, as to preserve the integrity of the transport/storage system: it should not be transported what cannot be stored.

Moreover, in order to maximise economies of scale and meet decarbonisation targets, CCS systems are being developed in (industrial) clusters (i.e. Hynet, Porthos, Acorn, just to name a few) where emitters of diverse industries (cement, fertilizer, steel, refinery, power, H₂ production, etc.) will be exporting its captured emissions to a common transport infrastructure (existing or purpose-built) for storage in depleted reservoirs, e.g. [3],[4],[5]. Here, the typical operating philosophy is to operate the transport pipeline at low pressure (in gas phase) and then, at some point as pressure builds up in the reservoir, transition to high pressure operation (liquid phase). Usually, the operator of the transport/storage

system will set the fluid specification to which all the emitters will have to meet. The emitter will then need to design its purification and conditioning system accordingly. Often, the transport operator will need to balance the diverse nature of the capture technologies as well as the costs for purification and the costs of design for undesirable species in the pipeline.

While the impurities content is controlled and measured, each emitter will be discharging its CO₂ at different compositions and the operator will be accepting it if it meets the specification. Therefore, the final composition to be transported and injected will contain, potentially, all the possible compounds associated to each capture and purification technology (i.e., solvents or other chemicals) or other compounds used in each individual industrial process. Thus, it is realistic to expect that more than 20 species of diverse chemical nature will be present in the mixture: a chemical cocktail. Additionally, temporal variations in the feed rate of the various emitters will result in variations of composition along the pipeline. These variations may have a (temporal) impact in the transport, injection, and storage of CO₂ [6].

In this work, we investigate the phase behaviour of a CO₂ mixture with more than 20 impurities. While the aim is to qualitatively identify the potential number of phases that could form, we focus on the potential issue of liquid dropout at low pressure conditions during gas phase operation.

2. Impact of Impurities in CO₂ streams

The effect of impurities in CO₂ streams, in general, is well documented, e.g., [7],[8],[9],[10],[11]. Their presence can lead to flow assurance, corrosion, integrity, safety, processing, economic and geological storage issues.

Understanding the thermo-physical and transport properties of the mixture is fundamental for the design and operation of all stages of CCS systems. It is often assumed that impurities less than 1000 ppm(v) do not “significantly” affect the properties of the fluid. Indeed, this might be the case (and assumption) in the design of pipeline transportation systems. However, it is noted that certain low molecular weight or light gases will have a particular strong impact in the physical properties (and, in consequence in the design and operation of CCS transport systems) even in small quantities (such as hydrogen, see e.g., [12],[13]).

The effect on impurities could be classified in two groups. The first group relates to the impurities related to the operation of the transport system at high pressure (liquid/supercritical). Here, the key impact is that some impurities open-up the two-phase region, in the pressure-temperature plane, leading to an increase of required operating pressure to ensure single phase flow. The second key group is related to the effect of the solubility of water (or other heavy components such as TEG) in the presence of impurities in CO₂. In order to avoid water (or any liquid) dropout, it is crucial to determine dew point of any liquid phase. In addition, it is important to determine the speciation in the liquid phases as particular impurities will increase (or decrease) corrosion risk.

2.1 Thermodynamic modelling of CO₂ mixtures

Several comprehensive reviews of thermodynamic models and their performance for CCS transport systems are available elsewhere and the reader is referred to them (e.g. [14],[15],[16],[17]). However, all these works address fluid equilibria of CO₂ mixtures with few light impurities. There is some thermodynamic modelling and validation for CO₂ with water and the effect of various gases (e.g. [18]), solubility of CO₂ in water with glycols or some amines (e.g., [19],[20]) or some ternary/quaternary/quinary mixtures of CO₂ with light/sour gases, water and TEG or amines (e.g., [21],[22]).

There is not a single universal Equation of State for use with CO₂ with all potential impurities (from non-condensable gases, polar components such as glycols, solvents such as amines or associating fluid such as methanol). While GERG-2008 (or EOS-CG/TREND) could be used for relatively simple CO₂ mixtures with some other gases and water, the EoS cannot support other component such as TEG or alcohols. In this scenario, cubic EoS with appropriate mixing rules (i.e., Huron-Vidal) or extensions to account for associating and solvation effects (for example, most notably Cubic-Plus-Association – CPA) seems more adequate. Other approaches that could be used up to certain extent are SAFT-based EoS.

Thus, the conventional approach to model CO₂ mixtures with a large set of components is to apply some empirical model reduction (mostly empirical) as to suit the final use (flow assurance, corrosion, reservoir, etc.) and use the most appropriate EoS. It is not a common practice to perform the thermodynamic modelling of the full set of CO₂ with impurities. In this work, we attempt to

investigate the phase behaviour of a CO₂ mixture with a large set of impurities.

3. Methodology and Basis

3.1 Equation of State (EoS)

All the computational experiments have been performed using Cubic-Plus-Association (CPA-Infochem) implemented in Multiflash v.7.1. In general, CPA covers well mixtures of CO₂ with non-condensable gases as well as other sour/acid gases. In addition, it can cover polar/associating effects induced by alcohols, glycols, and amines.

3.2 Unavailable Components in Multiflash Database

There are three components (α -aminoisobutyric acid, dimethyl sulphide – DMS, and potassium carbonate – K₂CO₃) that are not available in the Multiflash component library. These components were created using Symmetry Process Simulator and then exported into Multiflash.

3.3 Binary Interaction Parameters (BIPs)

The CPA EoS in Multiflash has already a large set of default BIPs that have been optimised against experimental data and these have been used (i.e., CO₂-water, CO₂-TEG, TEG-Water, MeOH-Water, MeOH-CO₂ to name few). All the default BIPs have been assumed. Additional BIPs have been added or modified as per Table 1. The default cross-association BIPs in Multiflash have been used.

Table 1: Non-zero BIPs added or modified in CPA EoS.

Pair	Value	Source
CO ₂ -Ar	0.18	[17]
CO ₂ -H ₂ S	0.106	
CO ₂ -O ₂	0.116	
CO ₂ -SO ₂	0.048	
CO ₂ -CO	-0.071	[23]
Water-Piperazine	-0.248	[24]

4. Phase Behaviour of CO₂ mixtures

Table 2 and Table 3 show the compositions of the two fluids considered in this work. Figure 1 and Figure 2 depict the corresponding phase diagrams of each CO₂-rich cocktail. Both compositions have the same impurities and amounts except that Cocktail 2 is TEG-free.

There are a few interesting features. Firstly, in Cocktail 1, it is seen that even a small addition of TEG is sufficient to induce liquid dropout at high temperatures (circa 70°C). A second liquid phase (MDEA-rich) is induced at lower temperatures (near critical temperature). In order to avoid any liquid dropout, at low pressures (or gas phase), the system would need to operate at temperatures higher than 70°C. Alternatively, the fluid would need to be TEG-free and, in this case, the operating temperature would need to be circa 30°C for liquid to appear (see Cocktail 2). In this scenario, there is not a ‘free’ liquid

dropout but two-phase equilibrium between liquid CO₂ dissolved in the MDEA phase in equilibrium with gaseous CO₂. For Cocktail 2, a ‘free’ liquid phase can appear at temperatures lower than -20°C.

A realistic operating condition of a low pressure pipeline at subsea ambient condition (i.e., 25 bar and 5°C) will likely see liquid dropout. However, the liquid fractions are expected to be significantly low (0.0005-0.0006% mol, see Figure 3). At relatively high velocities, the liquid may be transported in a mist/bubbly flow regime. Nevertheless, in the low points of the pipeline and, particularly at low flow conditions, this liquid could accumulate and lead to, for example, corrosion mechanisms. These liquid pools should be managed by pigging campaigns. The frequency will be dictated by how fast the liquid holdup will be built in the system.

O ₂	0.00000786533
H ₂ S	0.00000071254
SO ₂	0.00000235812
NO	0.00000011062
NO ₂	0.00000011062
EtOH	0.00000517203
HCN	0.00000071254
COS	0.00000041221
DMS	0.00000013459
α-aminoisobutyric acid	0.00000002886
K ₂ CO ₃	0.00000002886
Piperazine	0.00000112468
MDEA	0.00000241768
TEG	0.0

Table 2: Composition of Cocktail 1.

Component	Mol fraction
Water	0.00003434850
MeOH	0.00030863633
CO ₂	0.98948056152
H ₂	0.00231148724
Acetaldehyde	0.00000513430
Benzene	0.00000041221
CH ₄	0.00175477129
Ethane	0.00000772394
Propane	0.00000903478
Butane	0.00000382301
CO	0.00056379386
Ar	0.00000201998
N ₂	0.00549450240
O ₂	0.00000786533
H ₂ S	0.00000071254
SO ₂	0.00000235812
NO	0.00000011062
NO ₂	0.00000011062
EtOH	0.00000517203
HCN	0.00000071254
COS	0.00000041221
DMS	0.00000013459
α-aminoisobutyric acid	0.00000002886
K ₂ CO ₃	0.00000002886
Piperazine	0.00000112468
MDEA	0.00000241768
TEG	0.00000256197

Table 3: Composition of Cocktail 2.

Component	Mol fraction
Water	0.00003434850
MeOH	0.00030863633
CO ₂	0.98948312349
H ₂	0.00231148724
Acetaldehyde	0.00000513430
Benzene	0.00000041221
CH ₄	0.00175477129
Ethane	0.00000772394
Propane	0.00000903478
Butane	0.00000382301
CO	0.00056379386
Ar	0.00000201998
N ₂	0.00549450240

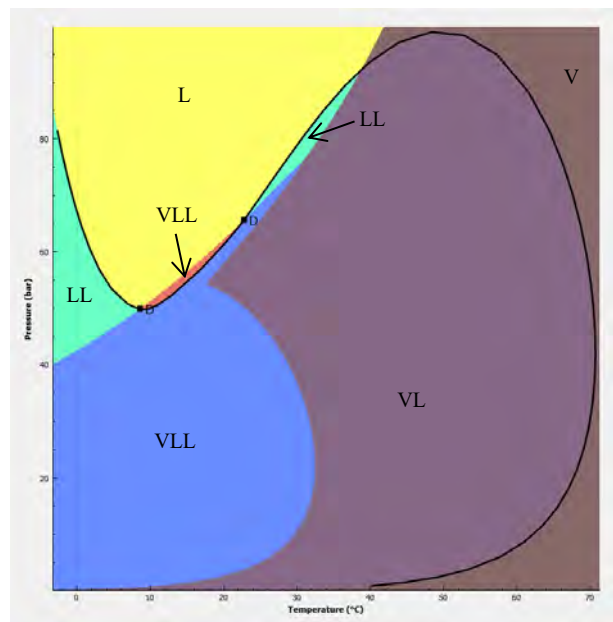


Figure 1: Phase Diagram for Cocktail 1.

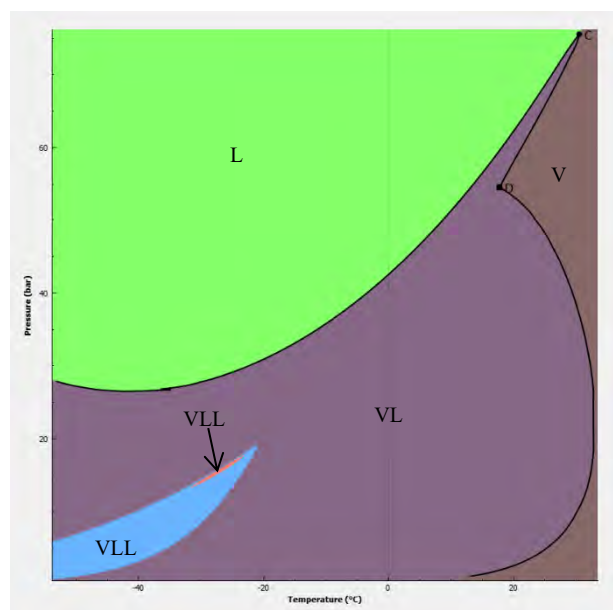


Figure 2: Phase Diagram for Cocktail 2. Note that solid phases (CO₂ and H₂O) are not shown (captured) by the thermodynamic model.

One could ask if the model is suitable to handle the solubility of CO₂ in TEG/water mixtures given the very low concentration of TEG. This is an important issue as if any liquid dropout is to be avoided (assuming low pressure operation), the TEG specification would need to be excessively low, thereby imposing severe constraints to the CO₂ emitters. Firstly, we assess the performance of the CPA EoS versus experimental data of a binary CO₂-TEG mixture. Figure 4 shows a (limited) comparison of the solubility of CO₂ in TEG. The experimental data has been taken from [25]. It is seen that there is good match at the relatively low pressures (which are the operating conditions of interest). This provides a good level of confidence in the thermodynamic model.

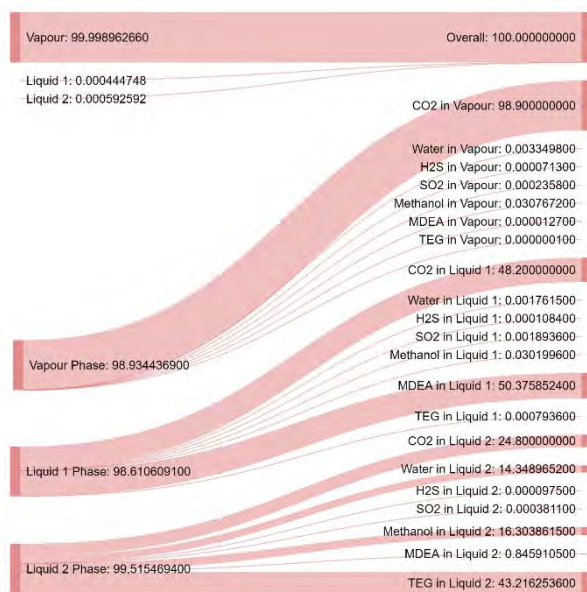


Figure 3: Phase and Component splitting of selected species at 25 bar and 5 °C in Cocktail 1. Amounts are given in mol %. Distribution of rest of components is not shown.

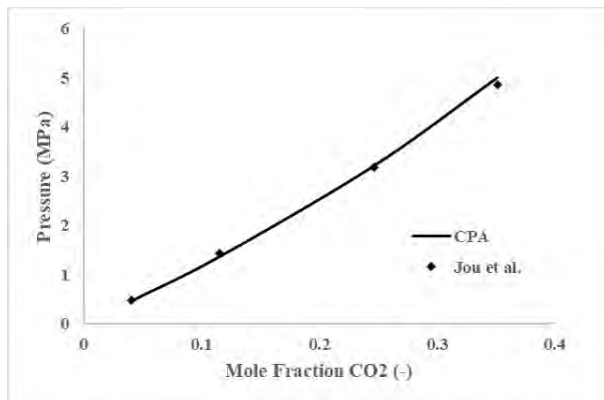


Figure 4: Comparison of CPA estimations and experimental data of CO₂ solubility in TEG at 298.15 K.

The comparisons performed in this work are of limited scope, one should also investigate the solubility of CO₂ in multicomponent systems, particularly in the presence of water, methanol, and amines (at very low

concentrations). These comparisons were not part of this study.

4. Discussion and Conclusions

It is reasonable to expect liquid dropout from impure gas CO₂ even with very small amounts of components such as water, TEG, amines, etc. At certain conditions, this liquid could be problematic inducing corrosion, erosion, or accumulation (holdup) in the pipeline. Thus, it is important to be able to determine the operating conditions and/or concentrations at which the liquid could dropout from the bulk.

It has been observed that a CO₂-rich fluid with low TEG content can induce liquid dropout at relatively high temperatures. It follows that for typical low pressure operating conditions and ambient condition, liquid dropout is a real possibility. The relative amount of liquid is very low and at high flowrate, the liquid may be transported in a misty/bubbly flow regime. Liquid accumulation (over a long period of time) at low flowrates should be managed with, for example, pig runs.

If there is a drive to avoid liquid dropout, in any foreseeable scenario, then a more onerous specification would be required. For example, the composition of Cocktail 3 (Table 4) will meet that requirement. Figure 5 shows the corresponding “exotic” phase diagram. It is seen that for low operating pressures there is no liquid dropout expected at temperatures above circa 5 °C (typical seabed ambient temperature). However, in case a depressurization scenario, it is possible that the system will experience liquid condensation, albeit temporal as it will vaporize back once system settles to ambient temperature. It is also noted that such diminute amounts could be problematic (and expensive) to technically achieve, detect and measure.

Table 4: Composition of Cocktail 3.

Component	Mol fraction
Water	0.0000070000
MeOH	0.0006100000
CO ₂	0.9892141038
H ₂	0.0023108790
Acetaldehyde	0.0000051330
Benzene	0.0000004121
CH ₄	0.0017543090
Ethane	0.0000077219
Propane	0.0000090324
Butane	0.0000038220
CO	0.0005636450
Ar	0.0000020195
N ₂	0.0054930560
O ₂	0.0000078633
H ₂ S	0.0000007124
SO ₂	0.0000023575
NO	0.0000001106
NO ₂	0.0000001106
EtOH	0.0000051707
HCN	0.0000007124
COS	0.0000004121
DMS	0.0000001346
α-aminoisobutyric acid	0.0000000289
K ₂ CO ₃	0.0000000289
Piperazine	0.0000011244
MDEA	0.0000000989

TEG	0.0000000014
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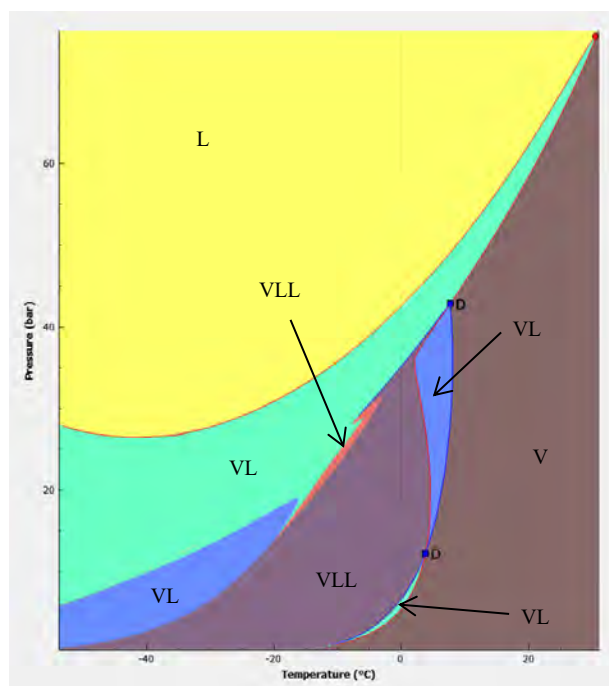


Figure 5: Phase Diagram for Cocktail 3.

The thermodynamic model used in this work is CPA (Infochem). The model has shown excellent prediction capabilities, in particular, for phase behaviour of polar and associating components. While there is a good degree of confidence in the model at high TEG concentrations, at low TEG concentrations there is some uncertainty that should be addressed (although we have shown good capability predictions). In addition, the CPA model does not have BIP for binary pairs with MDEA (although this does not seem to have a great impact, at least with the fluids considered in this work). It is also noted that the CPA model does not include association parameters between CO₂ and TEG to describe cross-association and solvation effects. This potentially has the largest effect and should be investigated in future work.

While there is wealth of data for many binary CO₂ mixtures of interest, there is lack of experimentation for truly multicomponent CO₂ mixtures. In order to reduce uncertainty, each transport operator would need to commission experimental campaigns to validate EoS models (with a large number of impurities) such the one presented in this work. Indeed, these experiments may be complicated and expensive to carry out. Joint-Industry Partnerships and collaborations (knowledge sharing) will be fundamental. We are currently working in the formation of one.

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