CO_2 Solubility Performance of Deep Eutectic Solvents (DES)

Water and Energy Workshop
Organized by Texas A&M University at Qatar

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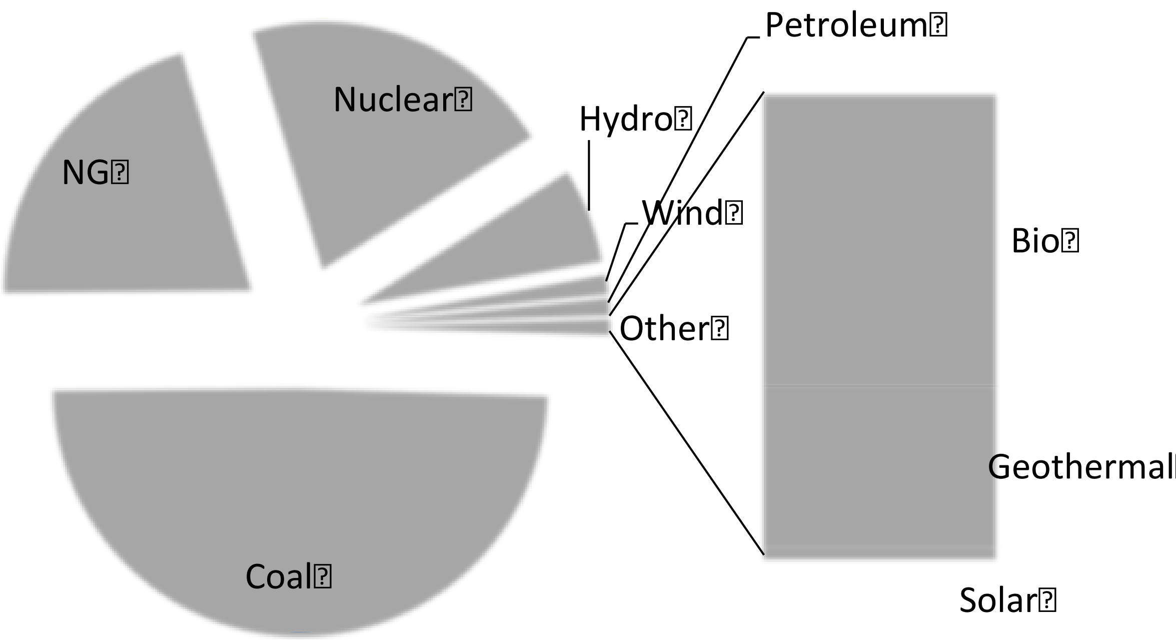
Doha, Qatar

Power Generation

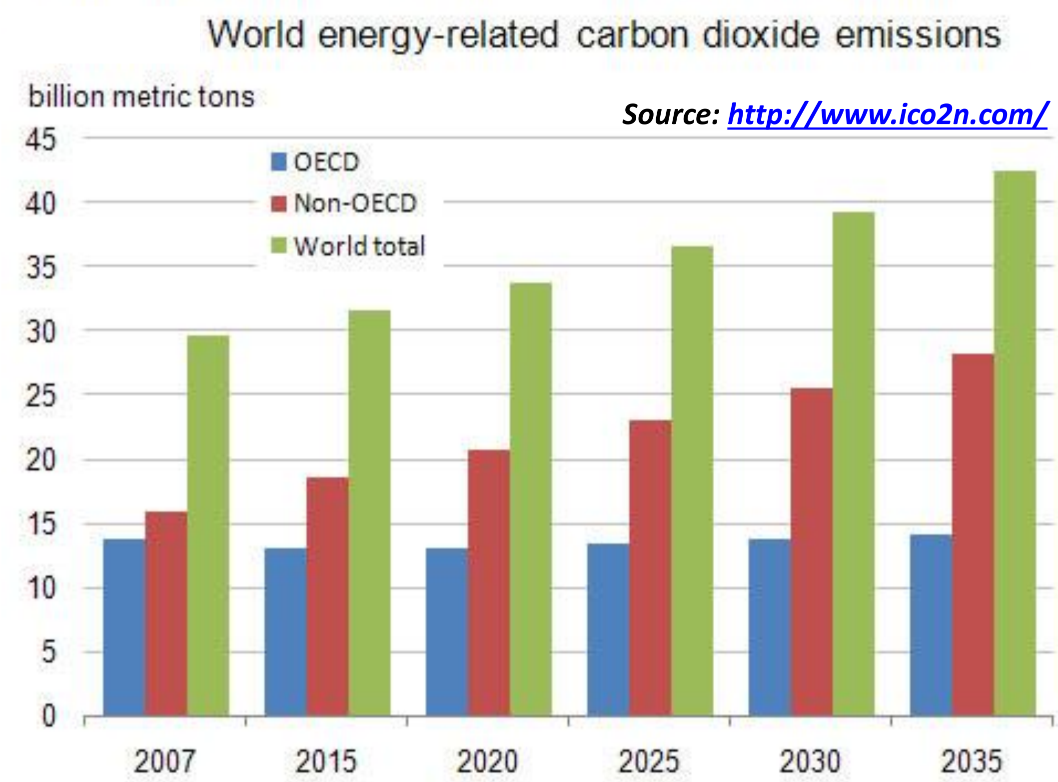
Sources as they apply to 24 hour

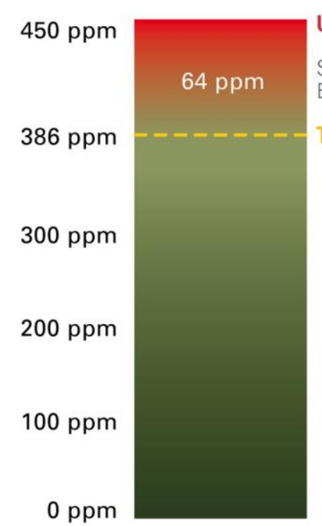


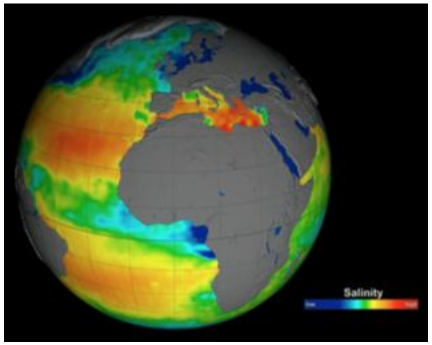
Coal	12 hours
Natural Gas	5 hours
Nuclear	5 hours
Hydropower	1.5 hours
Wind	18 minutes
Petroleum	16 minutes
Biomass	9 minutes
Geothermal	5 minutes
Solar	21 seconds

We're still heavily dependent on the fossil based fuels.
Consequent effects are gaseous emissions! Especially CO_2…

World Energy Related CO_2 Emissions





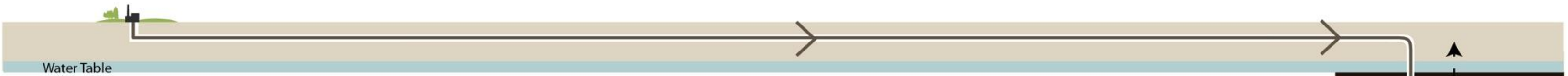


U.S. Energy Information Administration / International Energy Outlook 2012
OECD = Organization Economic Cooperation and Development member countries

Global energy use accounts for over 85% of the 37 Gt of CO2 released to the atmosphere annually

CC & ?

Emissions Source



CO_2 is transported using pipeline systems similar to those that have moved natural gas and oil for decades.

CAPTURE

CO_2 is captured from large emission sources, including:

- Coal-fired power plants,
- Oil and gas operations (including oil sands upgraders and refineries),
- Other industrial activities such as chemical, fertilizer and cement.

Carbon Capture and Storage (CCS) is a process designed to:

1. Capture carbon dioxide (CO_2) emissions from large industrial facilities before the CO_2 is emitted to the atmosphere,
2. Transport the CO_2 through pipelines, and
3. Permanently store the CO_2 in deep, secure underground rock formations.

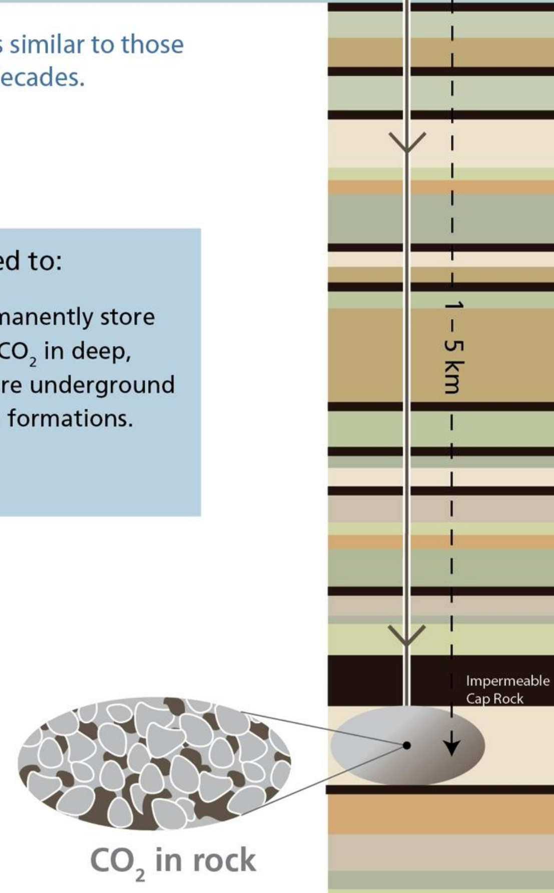
STORAGE

CO_2 is injected at a depth of 1 – 5 kilometres into deep underground rock formations where it is permanently stored. A barrier of impermeable rock and natural chemical interactions ensures long-term storage.

Geological formations used for storage include:

- Depleted oil or gas reservoirs
- Saline Formations
- Coal seams

*Not to scale



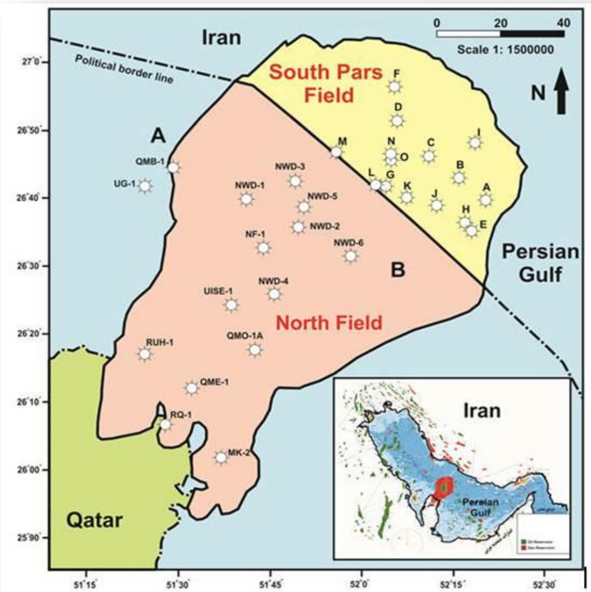
http://www.ico2n.com/

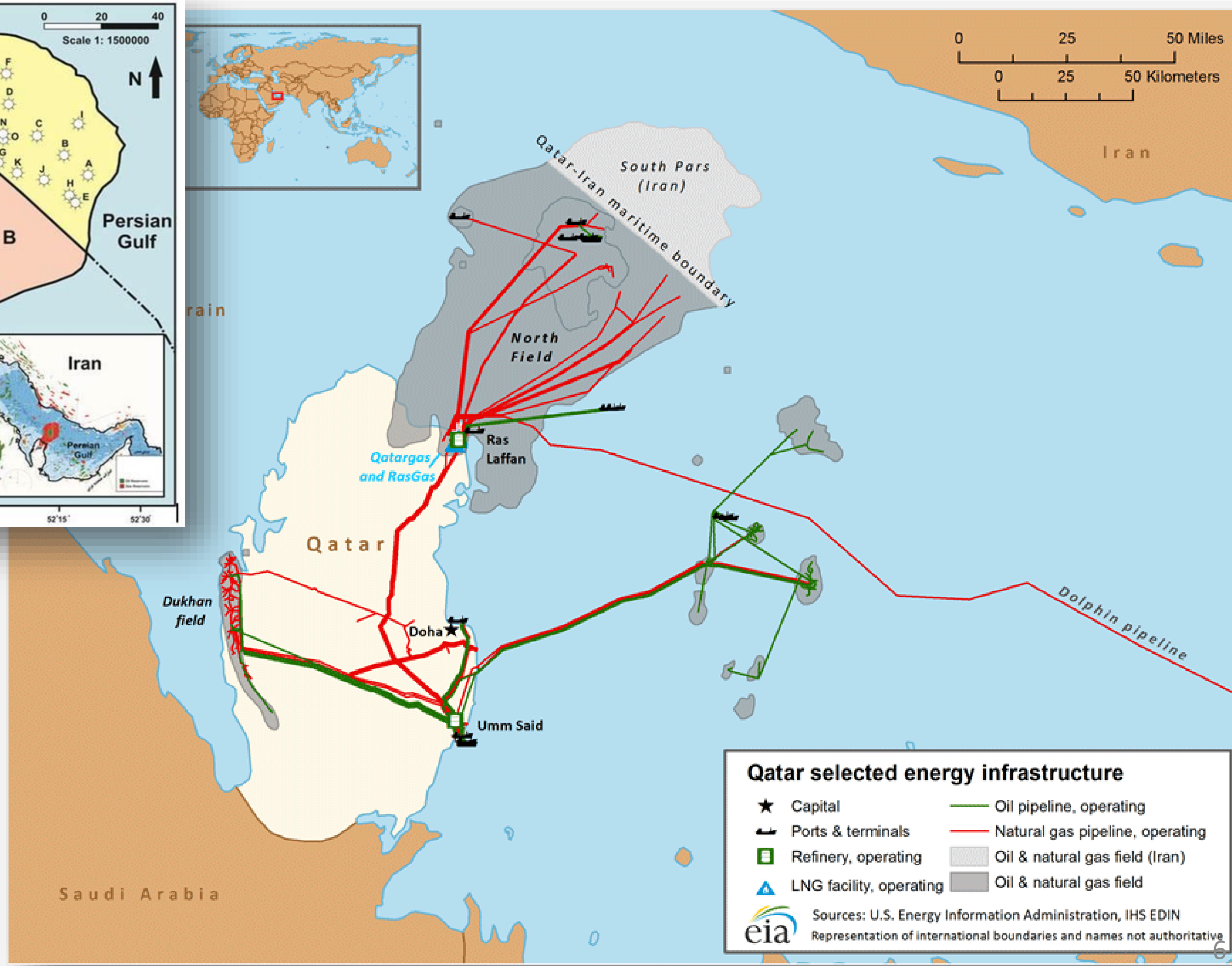
Problem(s)?

"If you are looking for a nice academic/industrial/environmental problem to work on,
CO_2 capture is a great one!"

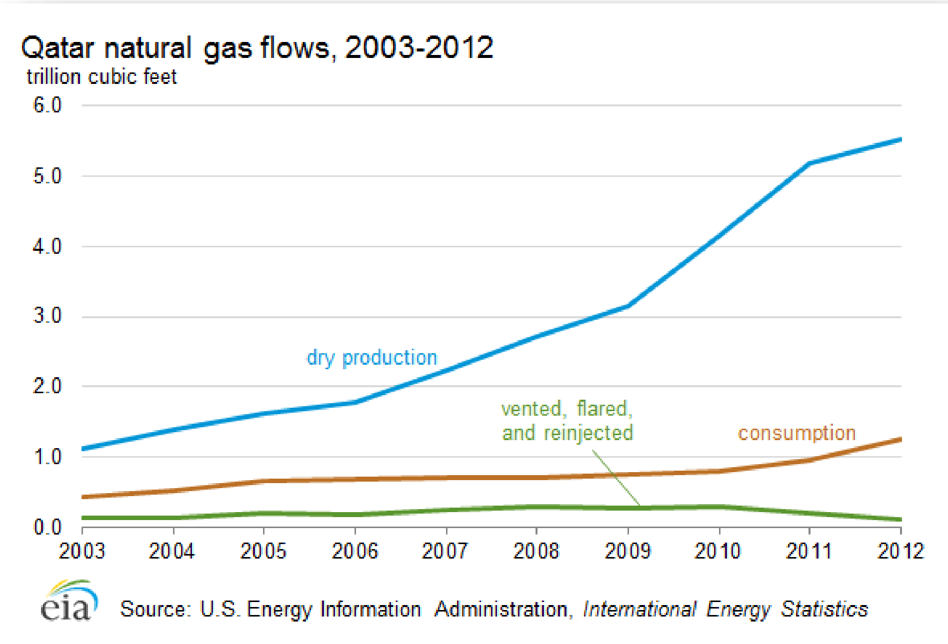
Paul Alisivatos & Michelle Buchanan

New/Recent Reservoirs Qatar North Field





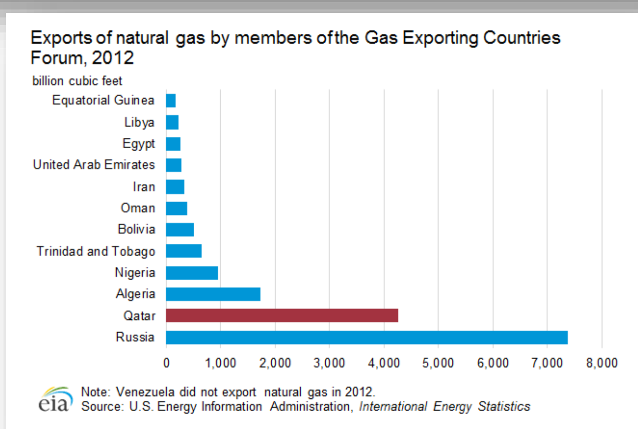
Qatar North Field



Basic Gas Facts - Qatar

Basic Gas Facts	2006	2007	2008	2009	2010
Gas reserves (bcm)	..	25620	25242	25366	25257
Gas production (mcm)	51556	61878	78306	89389	120568
Gas consumption (mcm)	17236	19232	20291	22921	23687
Gas imports (mcm)					
-Imports pipeline					
-Imports LNG					
Import dependency (%)*					
Gas exports (mcm)	33836	41516	57897	67425	96880
Natural gas supply per capita (toe)	..	..	..	..	..
Technically recoverable shale gas resources (bcm)	..	..	..	..	..
Coalbed methane resources (bcm)	..	..	..	..	..

c = confidential; - = nill; ..= not available
* Imports dependency of natural gas = (imports - exports) / consumption
Source: Natural Gas Information © OECD/IEA, 2011



Qatar's natural gas production rate
&
Qatar's proven reservoirs.

CO_2 Capture Perspective

Various Opinions: *Politicians vs. Academicians*

A Politician's definition of “Clean Energy”

Grand Challenges of the 21st Century

Environment

Greenhouse gases

◆ CO_2 levels will reach ~ 500 ppm by 2050 (460 ppm is the point of no return)

◆ Ocean floor has more carbon (in CH_4) than all fossil fuels combined

Sustainability

Accessible technologies

◆ Lack of accessible and sustainable technologies

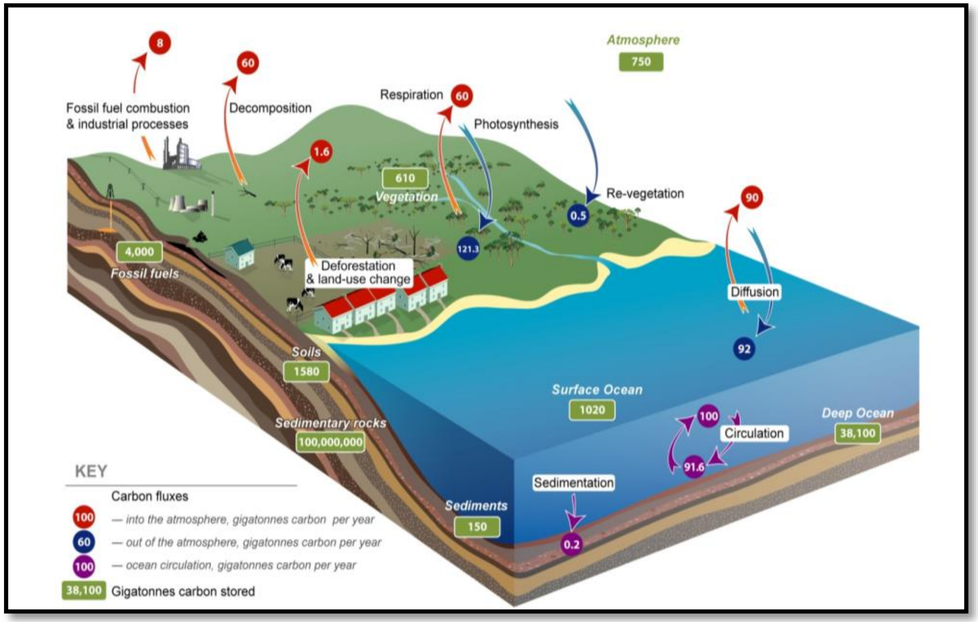
◆ Higher energy prices

◆ Expensive infrastructure maintenance

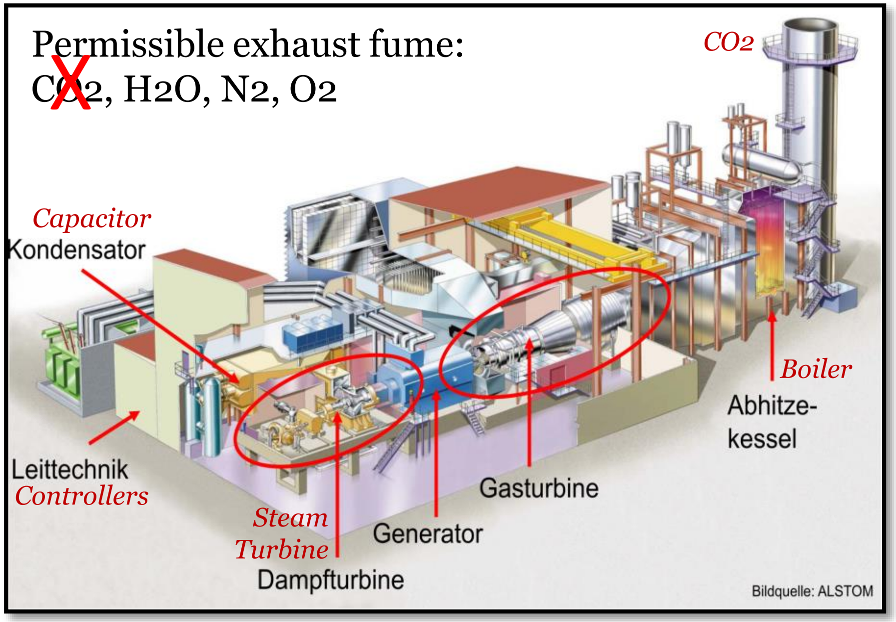
+ Energy
+ Water

Where is the problem?

Big Picture of the CO2 Cycle
human activity vs. nature activity



A modern day example
Dissecting a fossil fuel power plant

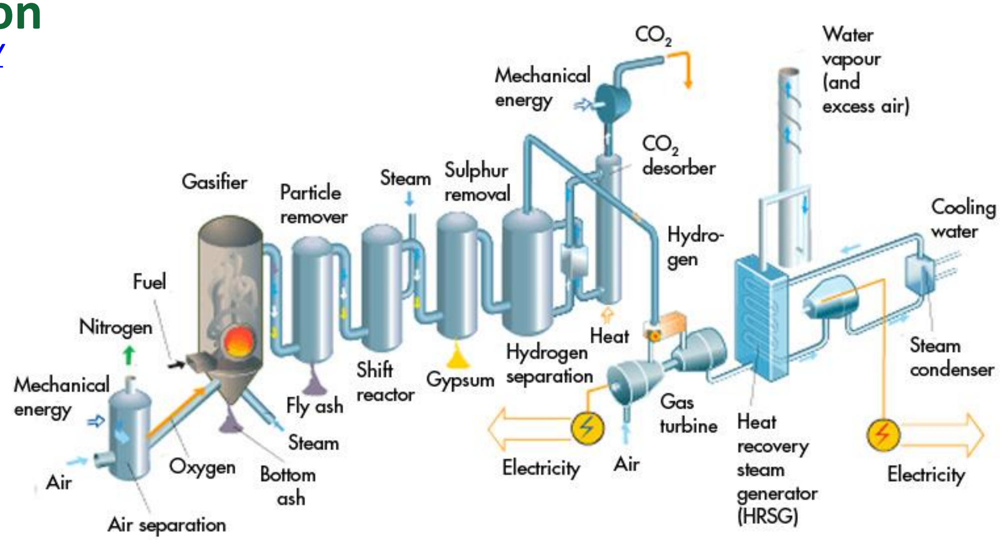


- **Target CO_2 capture locations:**
  - **Post combustion**
  - **Pre combustion**
- **Solving one problem shall not produce another problem**
- **Thermodynamically appreciable solutions**

Current Status

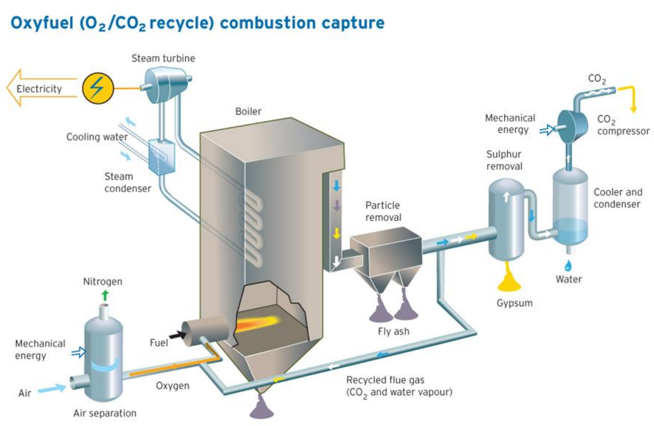
Pre-combustion

http://millicentmedia.com/



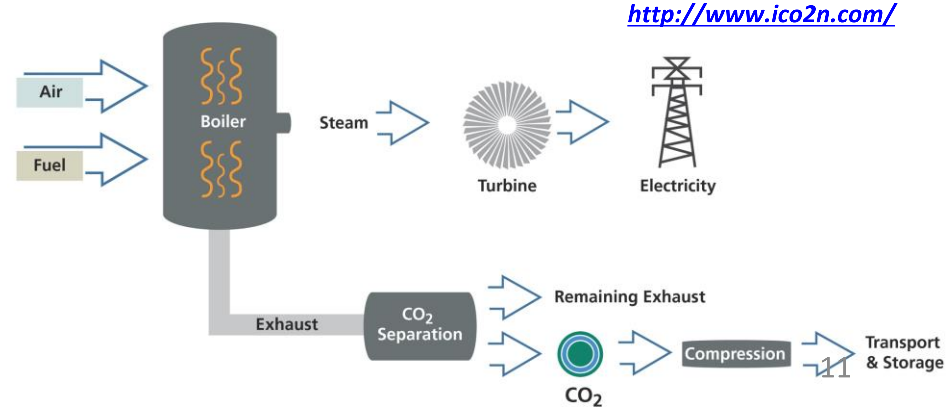
Oxy-Fuel

http://millicentmedia.com/

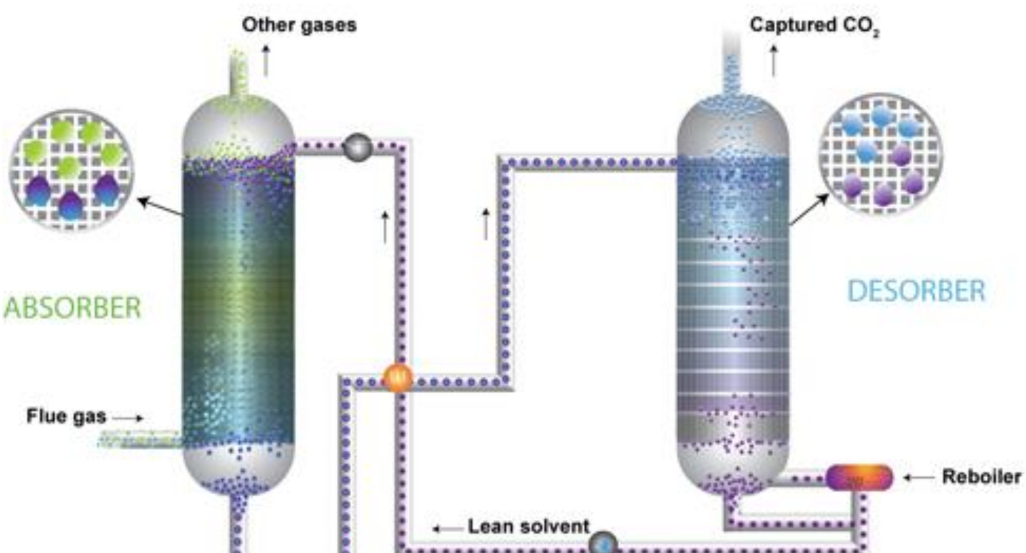


Post-combustion

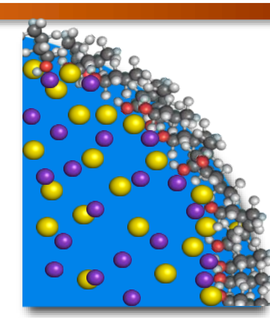
http://www.ico2n.com/



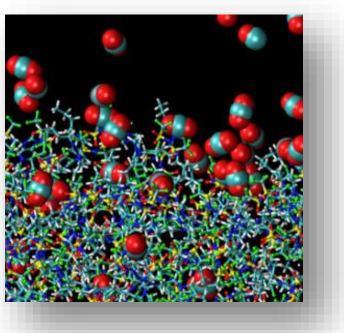
Chemical Engineers are conservative: Amines



http://www.co2crc.com.au/

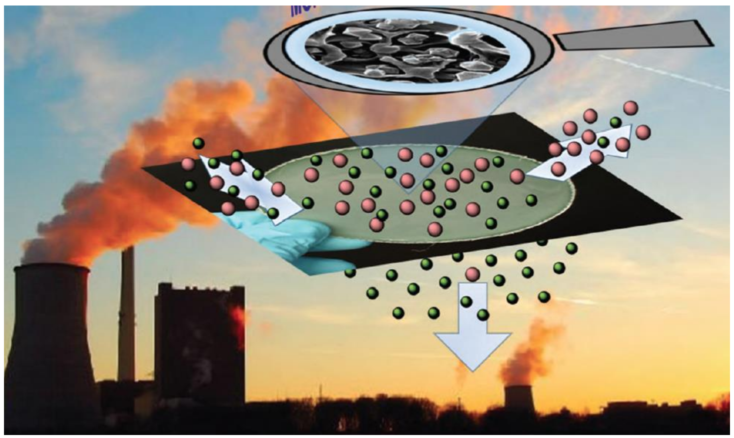


- Gas-liquid interface controls kinetic studies of structure and dynamics
- Can complex fluids be employed?

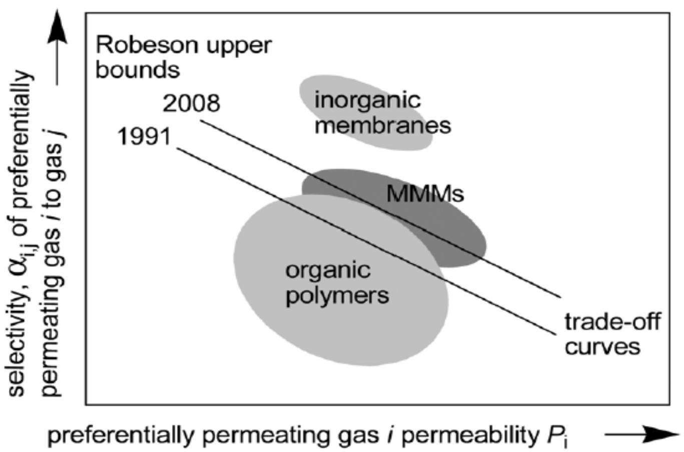


- Can the non-ideal solution behavior in mixtures be predicted and exploited?
- Can chemically / thermally stable materials be designed with high and reversible reactivity and specificity? Ionic Liquids…

Membranes



Dalton Transactions, 41 (46), 2012

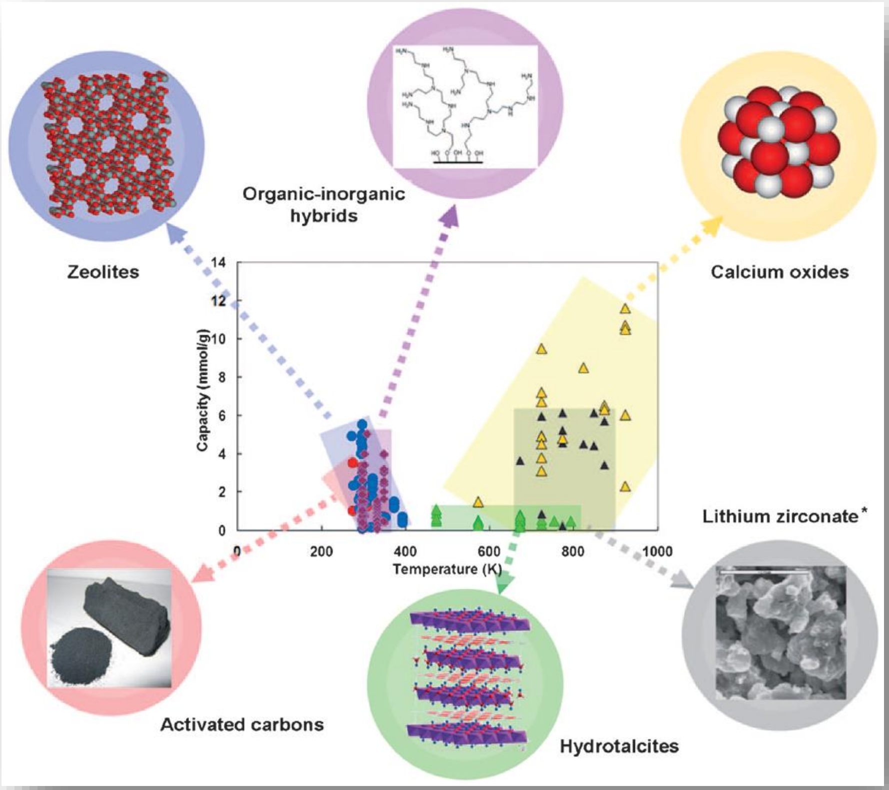


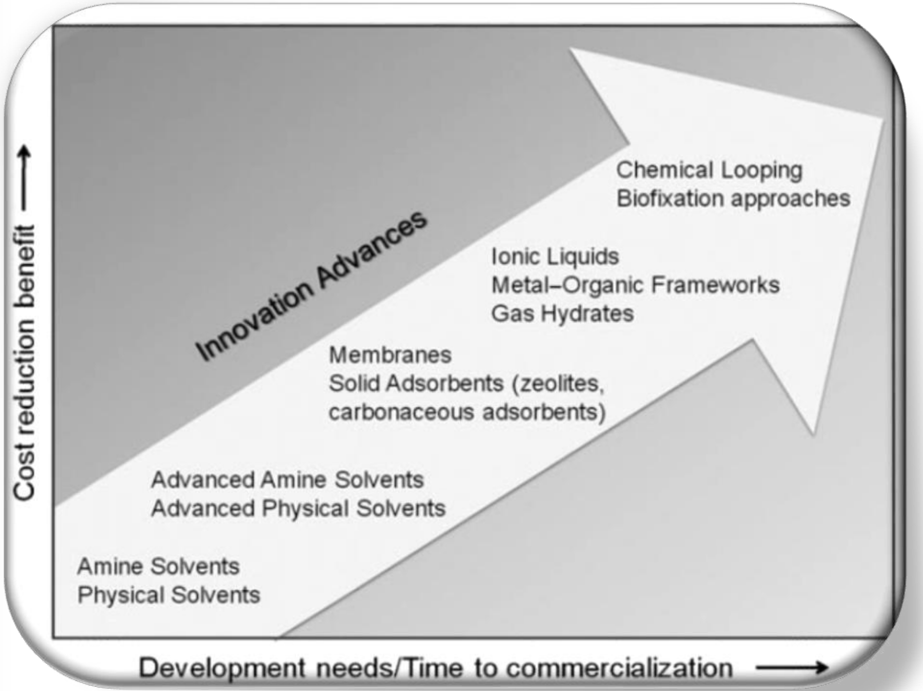
Robeson Plot

Schematic presentation of the trade-off between permeability and selectivity with the 1991 and 2008 Robeson upper bounds.

- Polymer membranes are used in many gas separation applications including natural gas treatment (removal of CO_2 before the natural gas can be passed to the pipeline)
- Separation based on selective permeation of targeted gas:
  - Selectivity based on relative solubility and diffusivity in membrane
  - Selectivity is not 100%
- **Trade-off on selectivity and permeability** (need to have both)
- Change in **pressure needed to drive separation**
- Can new materials be designed with nano-scale structures to enhance transport and selectivity?
- How can chemical and physical properties be used to design new membrane materials for **enhanced performance?**

Adsorbents: High Temperature & High Pressure





ChemSusChem 2009, 2, 796 – 854

Angew. Chem., 2010, 49, 6058 – 6082

CO_2 Solubility in Ionic Liquids at High Pressures

Imidazolium Based Ionic Liquids: Experimental and Simulation Approaches

Swelling effect on each ionic liquid was calculated and corrected.

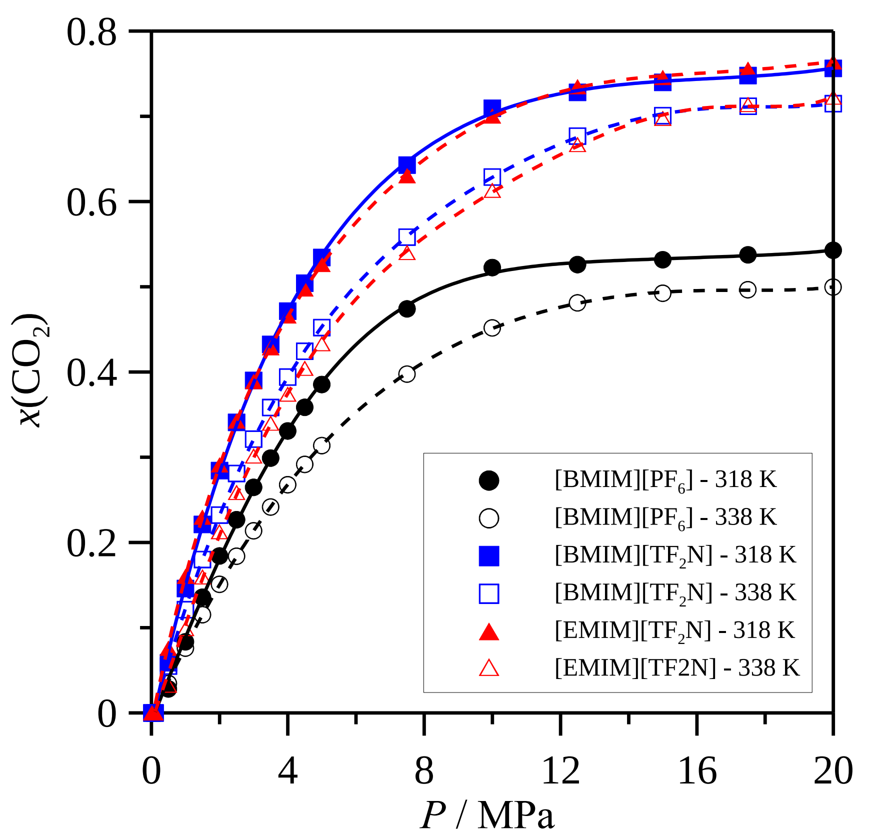
1-butyl-3-methylimidazolium hexafluophosphate, [bmim][PF_6],

1-ethyl-3-methylimidazolium bis[trifluoromethylsulfonyl]imide, [emim][Tf_2N]

1-butyl-3-methylimidazolium bis[trifluoromethylsulfonyl]imide, [bmim][Tf_2N]

Isothermal experimental solubility data of CO_2 in the studied ionic liquids.

Swelling corrected for high pressure CO_2 absorption data.



Fluid Phase Equilibria, 2013, 74-86 (351)
J. Phys. Chem. B, 2012, 116 (30), pp 9171–9185
J. Phys. Chem. C, 2012, 116 (22), pp 12055–12065
J. Phys. Chem. B, 2011, 115 (43), pp 12499–12513
Energy Fuels, 2010, 24 (11), pp 5817–5828
Energy Fuels, 2010, 24 (9), pp 4989–5001
Ind. Eng. Chem. Res., 2010, 49 (20), pp 9580–9595

Issues with Ionic Liquid Utilization

- Still very expensive
- Needs bulk production for making them economically attractive
- High viscosity – pumping issues
- Limitations in mass transfer
- Florination might be an issue with some anions

Alternatives???

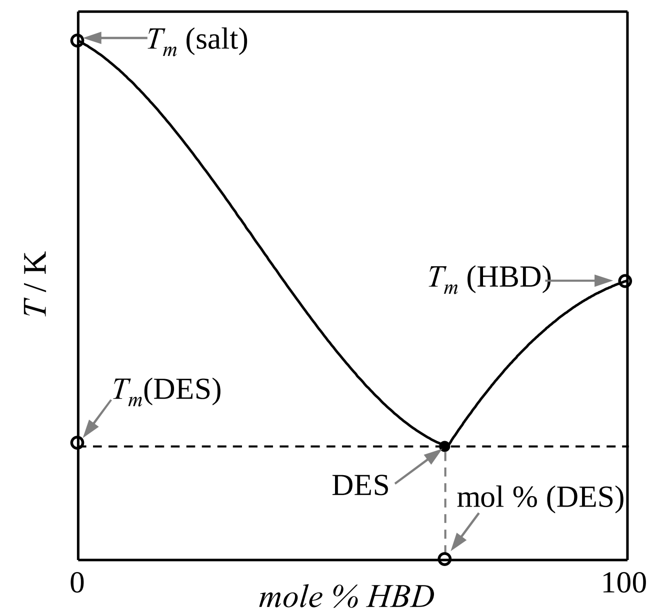
Deep Eutectic Solvents (DES)

Definition

- Deep Eutectic Solvents (DES) are a mixture of 2 or more components with a melting point lower than either of its individual components.
- DES are obtained by mixing a quaternary ammonium halide salt, an hydrogen bond acceptor (HBA), with an hydrogen bond donor (HBD) molecule, which should be able to form a complex with the halide, leading a significant depression of the freezing point.

Deep Eutectic Solvents (DES)

- Mixture of 2 compounds that has the lowest melting point
- Depression of freezing point related to the strength of interaction between the 2 components



Schematic solid-liquid phase diagram for a binary mixture between a salt and an HBD, showing the appearance of DES at the mixture composition and temperature remarked in the Figure. T_m stands for melting point. Solid line shows the melting point temperature as a function of mixture composition, dashed lines shows the temperature and composition of the eutectic mixture.

cation + anion + complexing agent ↔cation + complex anion
or
cation + anion + complexing agent ↔complex cation + anion

Deep Eutectic Solvents (DES)

- DES provide other interesting advantages in comparison with pure ILs, such as the fact that DES preparation may be carried out with 100% atom economy.
- DES can be also obtained from natural sources, so-called Natural DES, particularly through primary metabolites such as organic acids, amino-acids, and sugars.

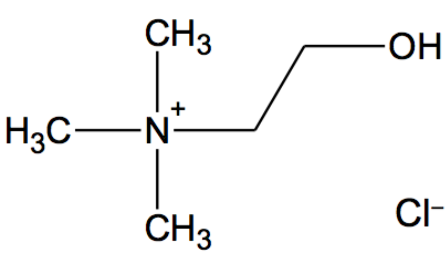
Objective(s): We're after

- Low cost
- High solute solubility
- Wide potential window
- Environmental compatibility
- No registration requirements

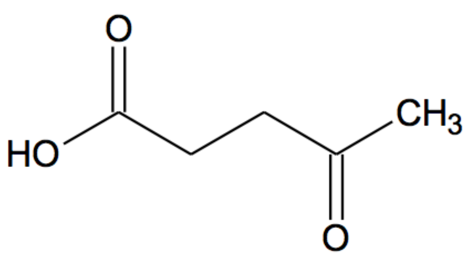
Solvents to substitute the current state-of-the-art in CO_2 capture.

Choline Chloride + Levulinic Acid

- [CH][Cl] is a non-toxic, fully biodegradable compound, which can be obtained at very low cost
  - Vitamin B4 RDA – 550mg
  - Produced on Mt scale (chicken feed additive) hence costs about 2 Euro/kg
- Levulinic acid (LEV) is a compound fully biodegradable, non-toxic, that may be obtained from biomass at low costs



[CH][Cl]



levulinic acid

Components

- The available studies on CO_2 capture using [CH][Cl] – based DES are mostly limited to systems such as urea, glycerol, ethyleneglycol or carboxylic acids such as malonic or lactic.
- But no studies for DES involving LEV are reported
- Molar mixing ratio: 1:2 (*more will be experimented soon*)

Physical Properties - Density

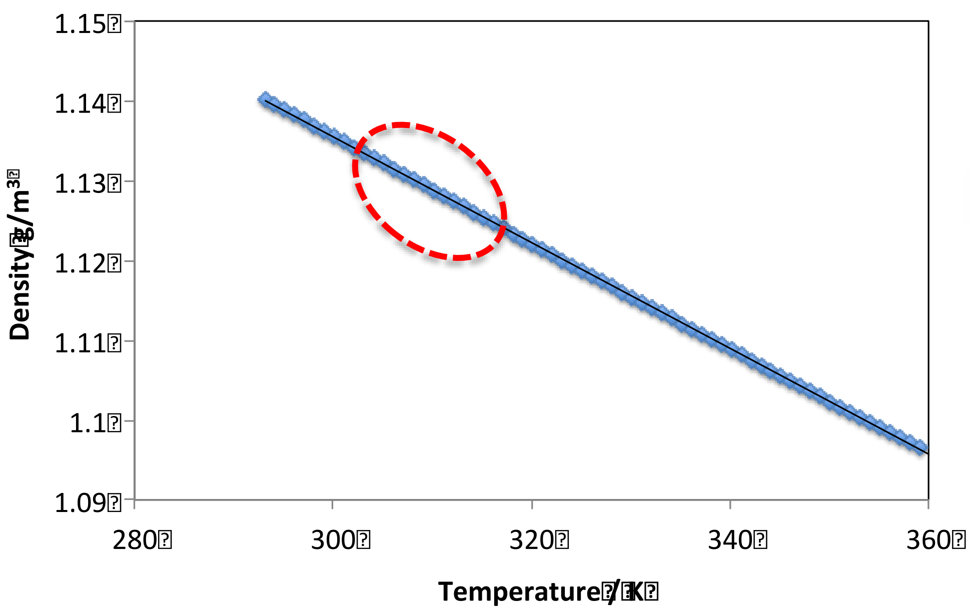
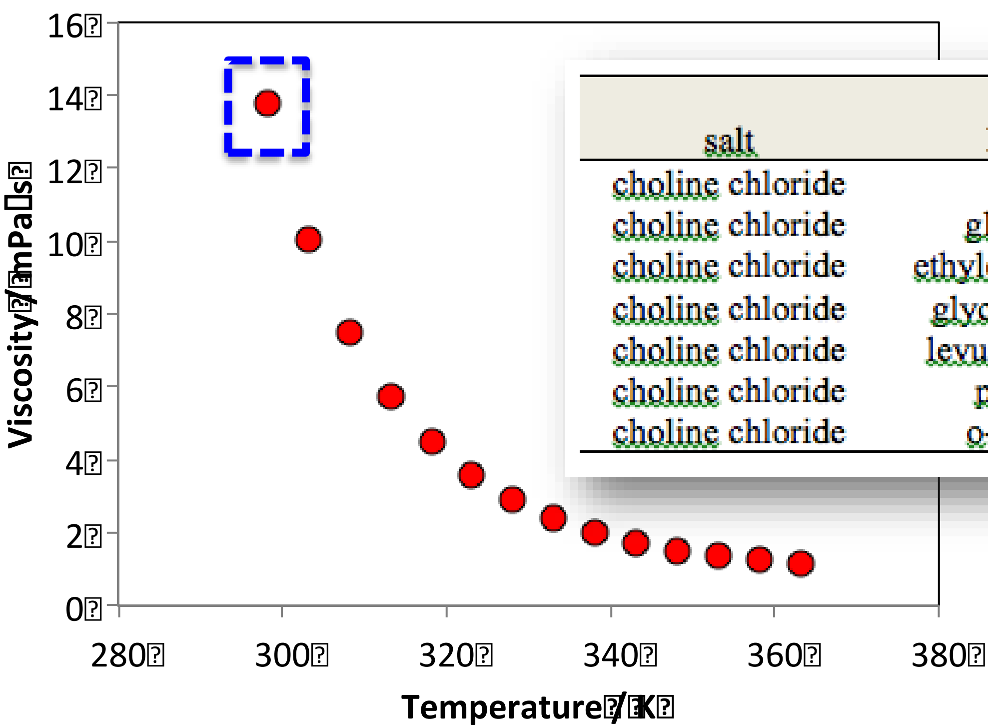


Table. Density, ρ, for CH_Cl + urea, 1:2 molar ratio

T / K	ρ / g cm^{-3}	sample origin	method
313.15	1.24	prepared	not stated
298.15	1.25	commercial	not stated
298.15	1.212	prepared	vibrating tube
298.15	1.1979	commercial	vibrating tube
313.15	1.1893	commercial	vibrating tube
313.15	1.1887	commercial	vibrating tube
298.15	1.20	prepared	tensiometer

Figure. Experimental density data for [CH][CL]+[LEV] 1:2 system at 1 atm (data obtained from Anton Paar® DM4500 Apparatus)

Physical Properties - Viscosity



salt	HBD	salt:HBD molar ratio	*T* / K	η / mPa×s
choline chloride	urea	1:2	303.15	449
choline chloride	glycerol	1:2	303.15	246.79
choline chloride	ethylene glycol	1:2	303.15	35
choline chloride	glycolic acid	1:1	303.15	394.8
choline chloride	levulinic acid	1:2	303.15	164.5
choline chloride	phenol	1:3	303.15	35.17
choline chloride	o-cresol	1:3	298.15	77.65

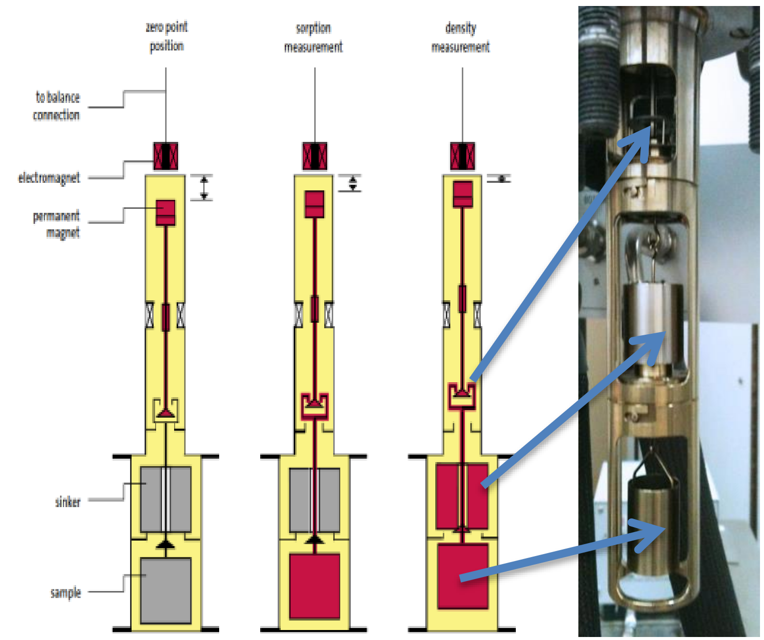
Much lower viscosity is obtained when compared with similar DES systems made by using [Ch][Cl].

CO_2 Solubility Measurements

- We used Rubotherm® sate-of-the-art gas sorption apparatus.
- Two isotherms are used: 25 °C and 50 °C
- Pressure measurements have been collected up to 30 bar with 5 bar increments.
- Buoyancy correction has been taken care of.

Gas Solubility Apparatus

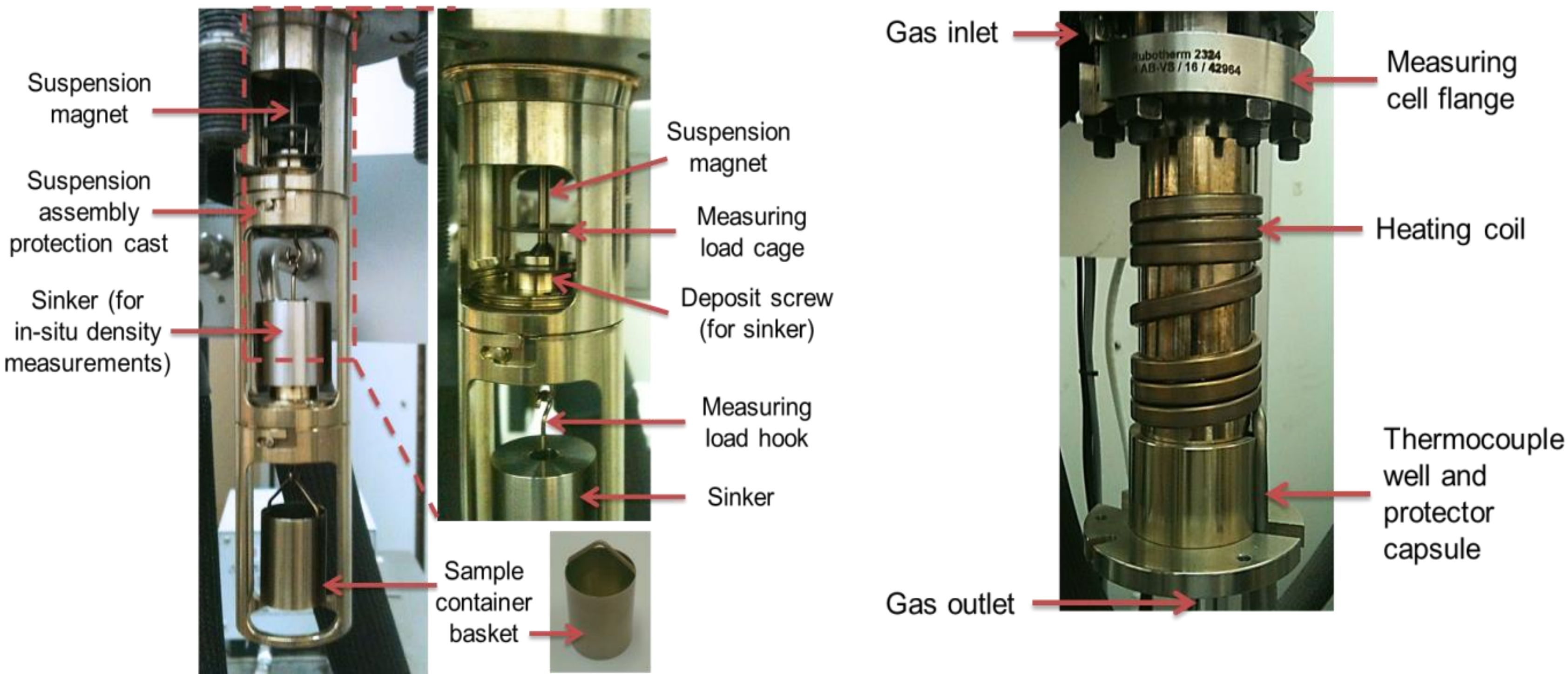
Thermodynamics
Energy & Environment



Rubotherm ® Magnetic Suspension Balance Assembly Atilhan Lab, Qatar University

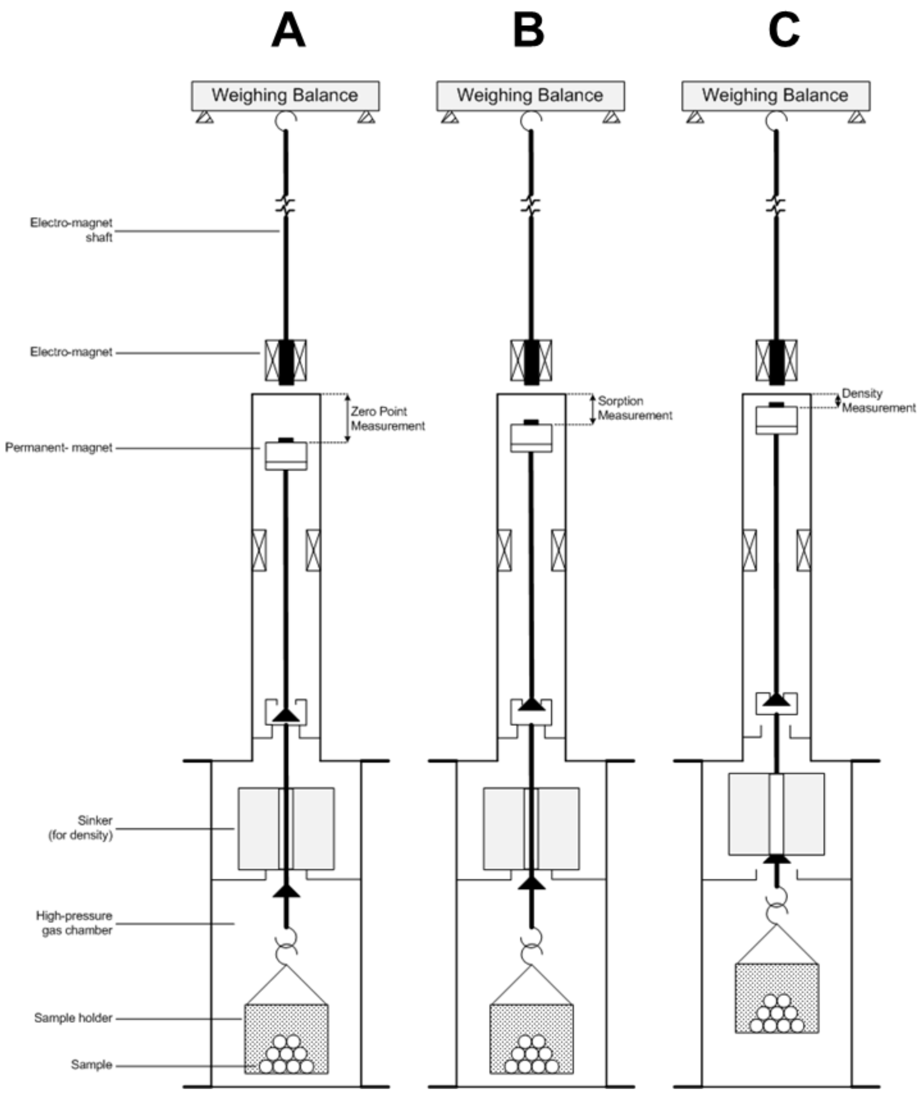
Rubotherm ® GmBH
Magnetic Suspension Sorption Apparatus (top-left)
Magnetic Suspension Thermal Analyzer (bottom-left – Gas Processing Center, Qatar University)

High Pressure Sorption Cell



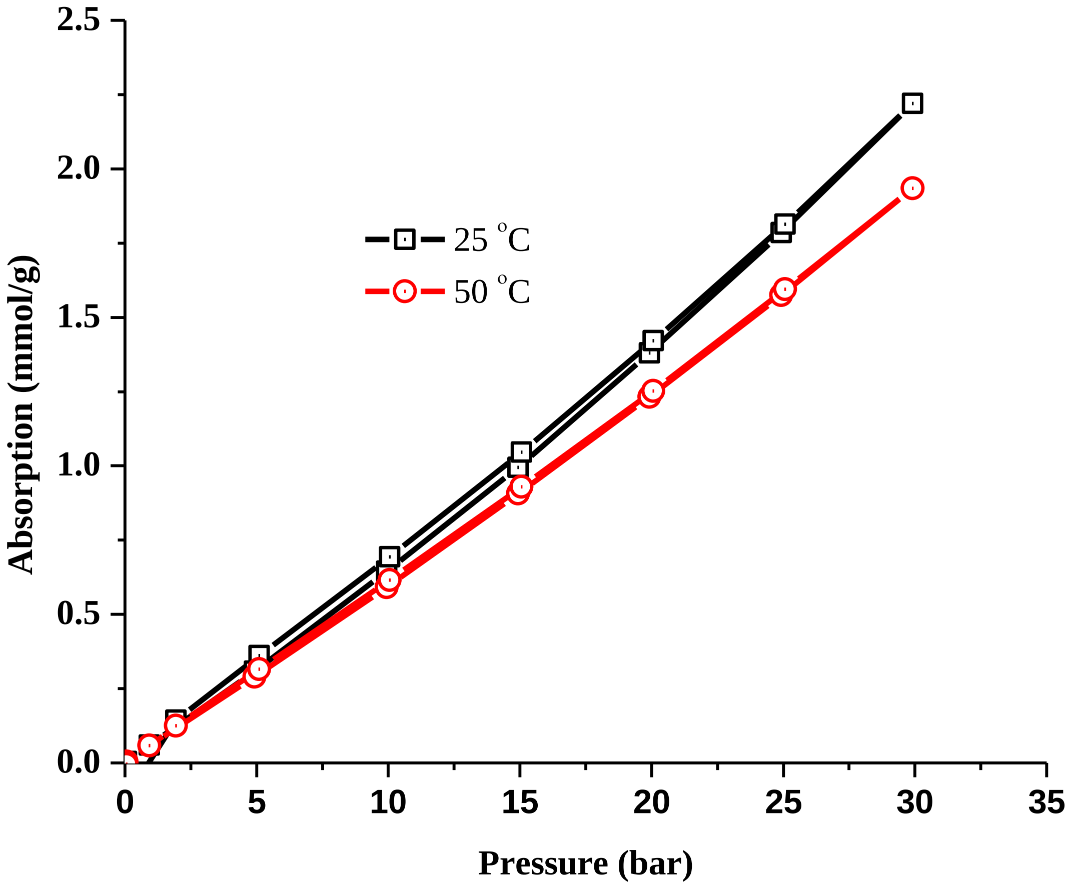
Rubotherm® Magnetic Suspension Balance (MSB). Photos of the magnetic suspension assembly, sample container basket, measuring cell and the magnetic coupling housing.

Operating Principle

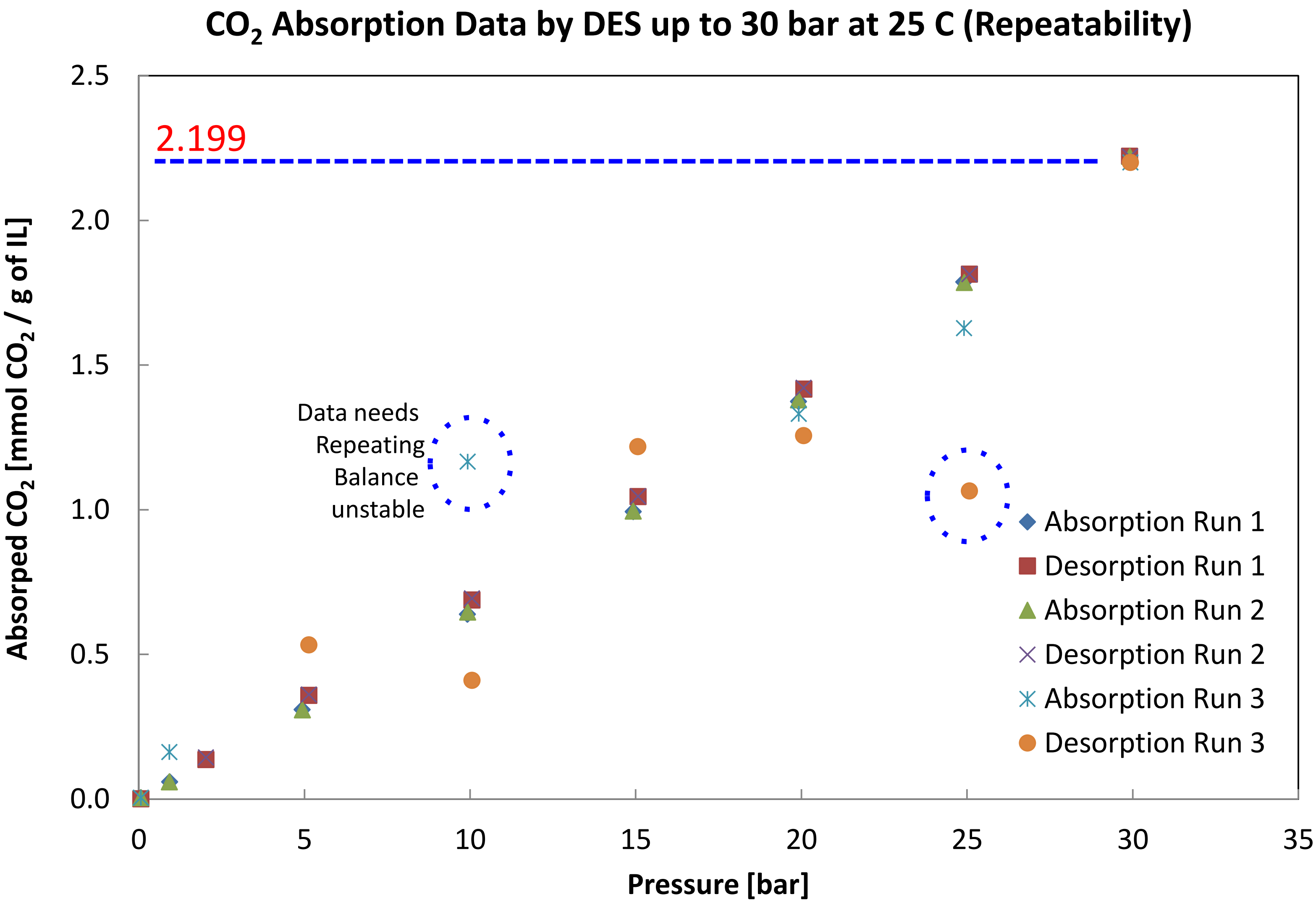


Schematics of magnetic suspension sorption apparatus operating principle. (**A**) sample loaded to measuring basket in high pressure cell; (**B**) Measurement point 1 (MP1) – magnetic coupling is on and mass of the sample is measured; (**C**) Measurement point 2 (MP2) – in–situ density of the adsorbed gas is measured.

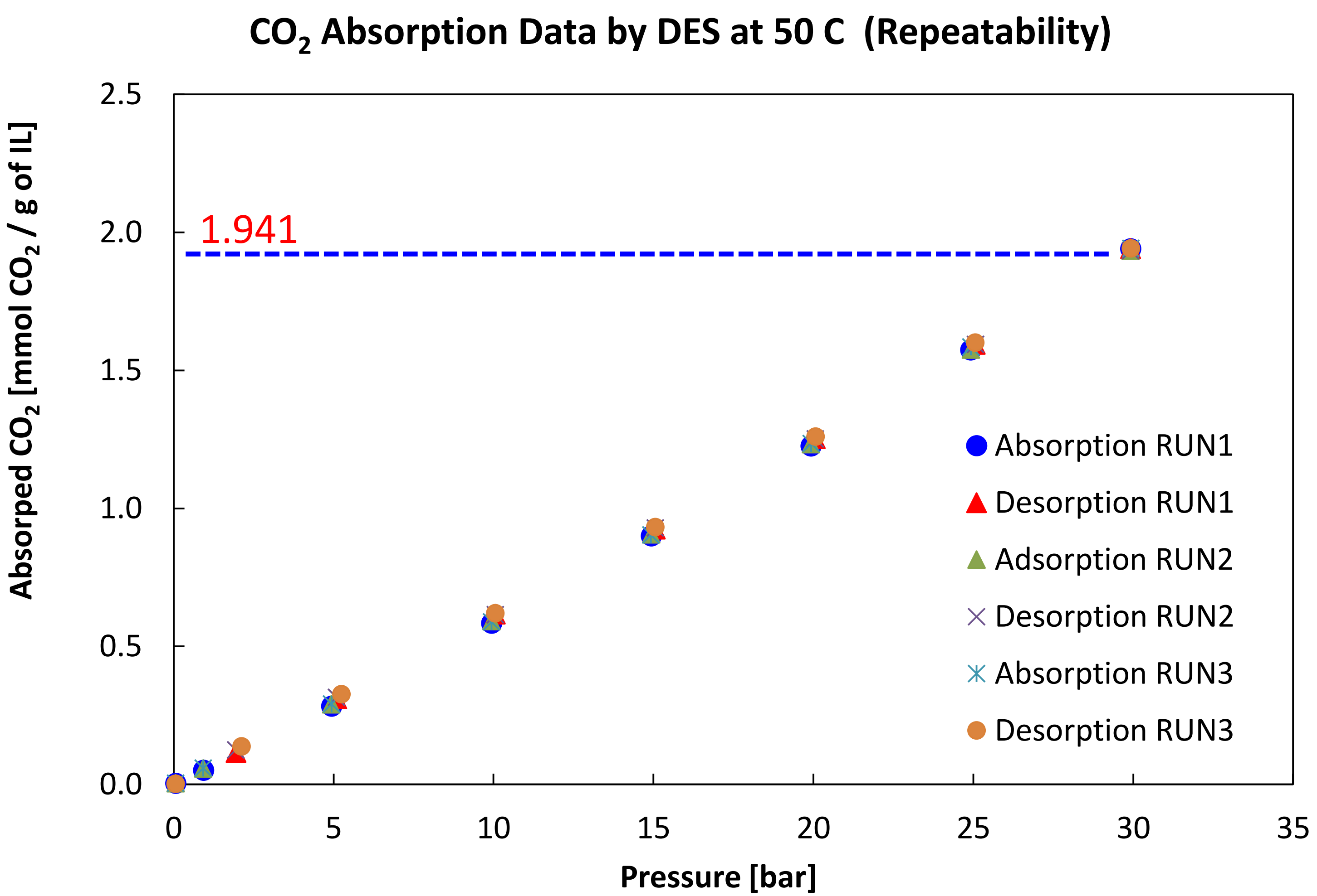
CO_2 Solubility Data – 25°C



CO_2 Solubility Data – 25°C (Repeatability)



CO_2 Solubility Data – 50°C (Repeatability)

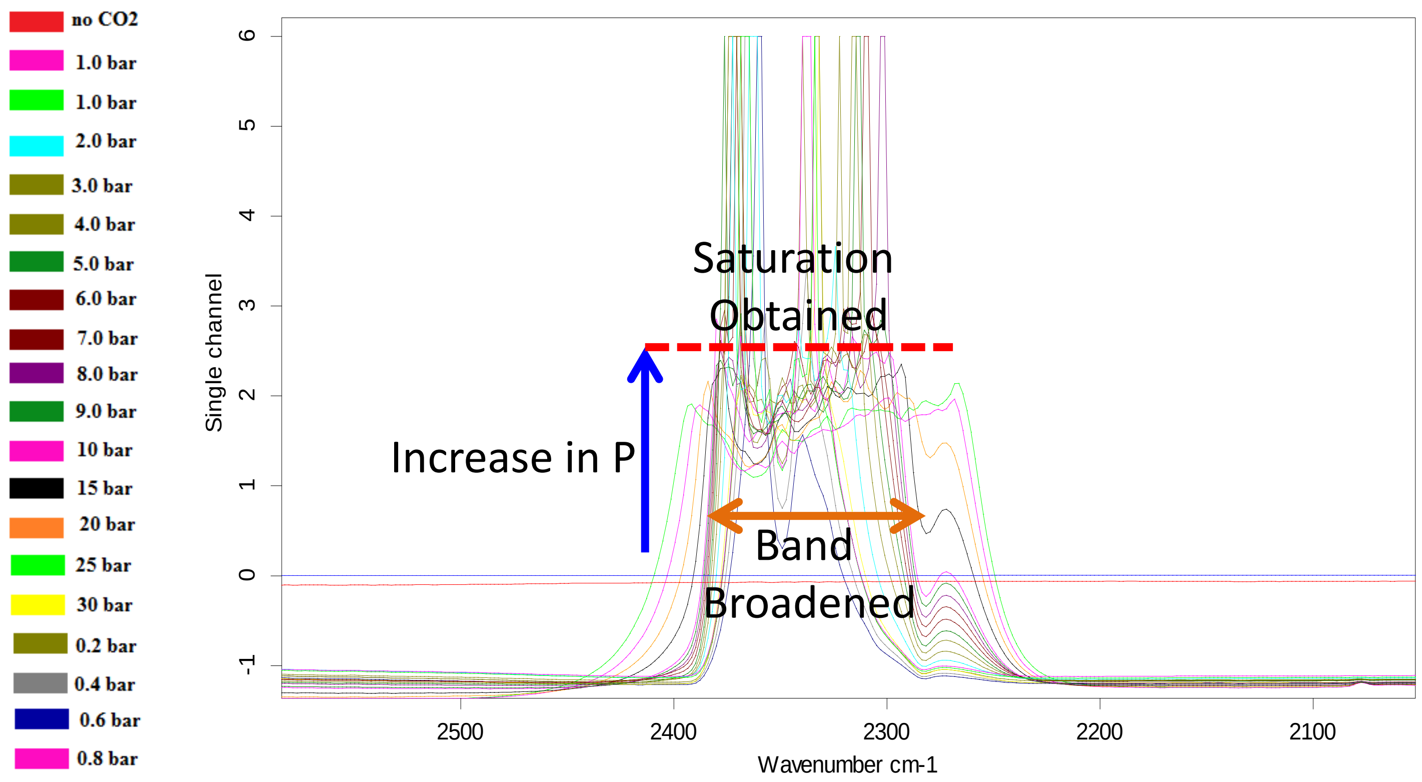


Comparison w/ Previous Studies

	Componentes of DES			Absorbate	Solubility	*T* / *P* (K/bar)
	IL	HBD	Molar Ratio			
This work	choline chloride	levulinic acid	1:2	CO_2	2.199 mmol/g	298 / 30
This work	choline chloride	levulinic acid	1:2	CO_2	1.941 mmol/g	323 / 30
Literature	choline chloride	urea	1:2	CO_2	3.559 mmol/g	303.15 / 60
Literature	choline chloride	ethylene glycol	1:2	CO_2	3.1265 mmol/g	303.15 / 60
Literature	choline chloride	ethanole amine	1:6	CO_2	0.0749 mmol/g	298 / 10
Literature	choline chloride	triethylene glycol	4:1	CO_2	0.1941 mmol/g	293 / 5
Literature	choline chloride	phenol	4:1	CO_2	0.2108 mmol/g	293 / 5
Literature	choline chloride	diethylene glycol	4:1	CO_2	4.204 mmol/g	293 / 5
Literature	choline chloride	glycerol	1:1	SO_2	0.678 g /g	290 / 1
Literature	choline chloride	2,3-butanediol	1:4	CO_2	0.426 mmol/g	298 / 5
Literature	choline chloride	1,4-butanediol	1:3	CO_2	0.372 mmol/g	298 / 5
Literature	choline chloride	1,2-propanediol	1:3	CO_2	0.374 mmol/g	298 / 5
Literature	choline chloride	lactic acid	1:2	CO_2	0.562 mmol/g	348 / 20

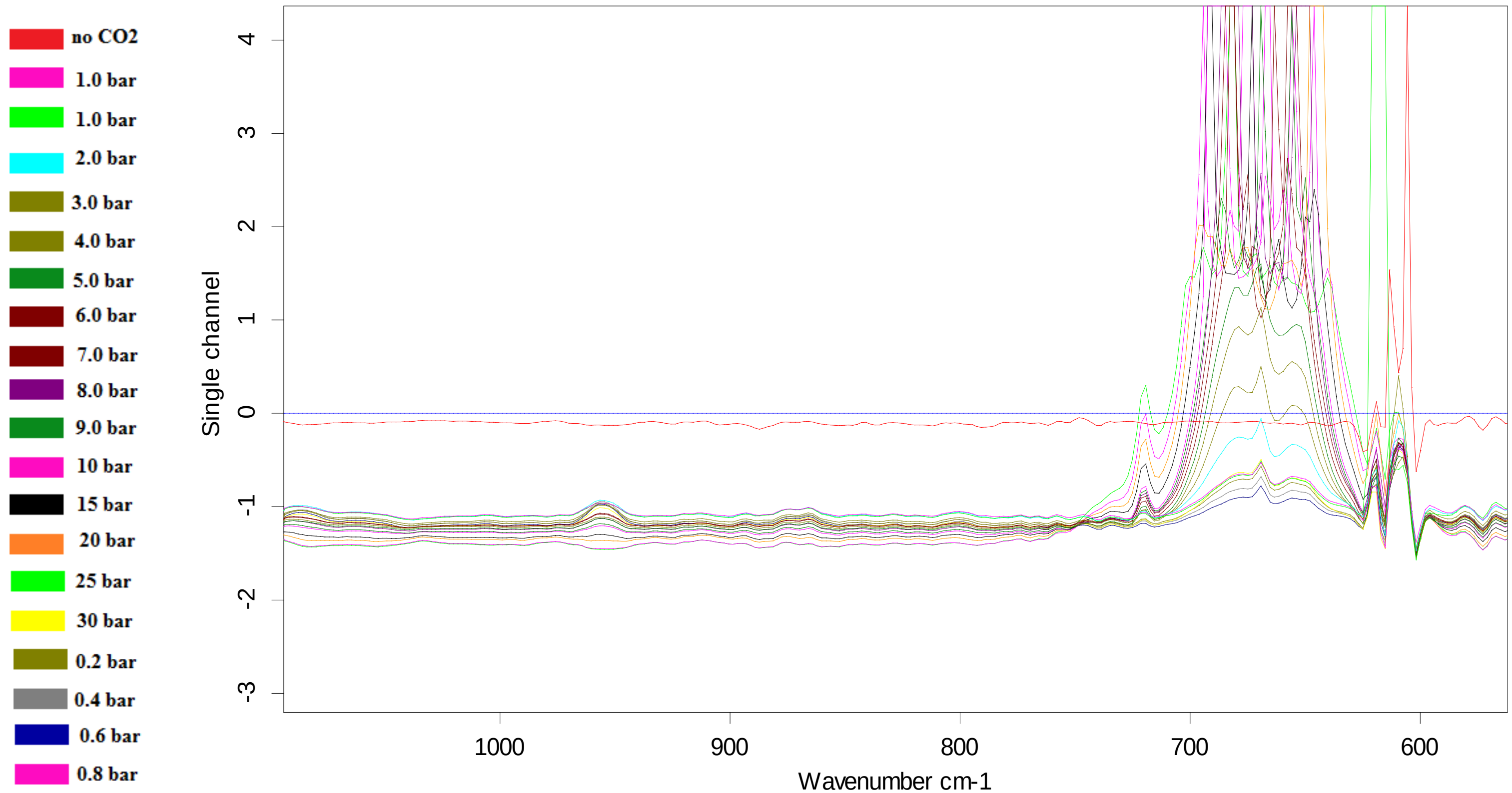
In-Situ FTIR Measurements

Asymmetric Stretch of CO_2 at (2300 to 2400) cm^{-1} band



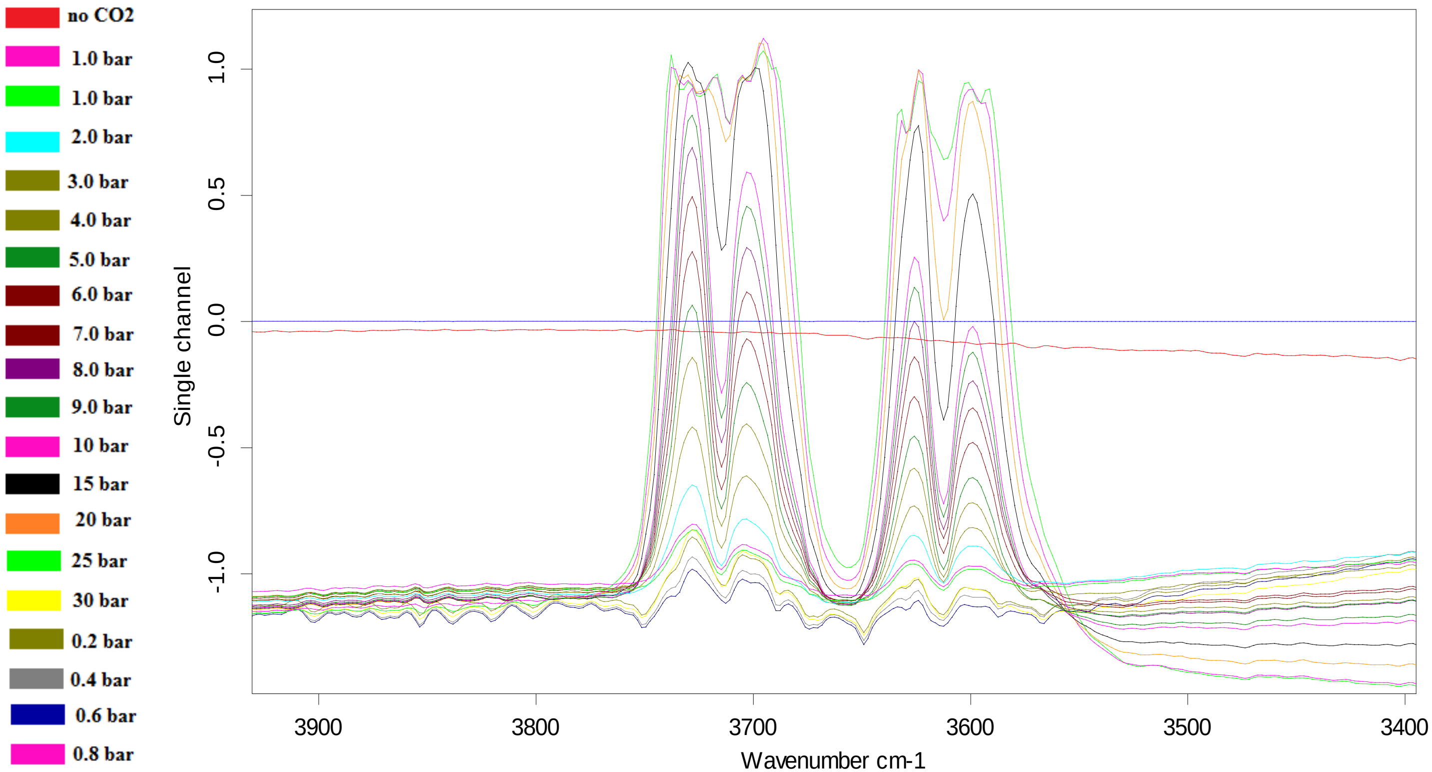
In-Situ FTIR Measurements

Vertical Bend of CO_2 at (700 to 800) cm^{-1} band



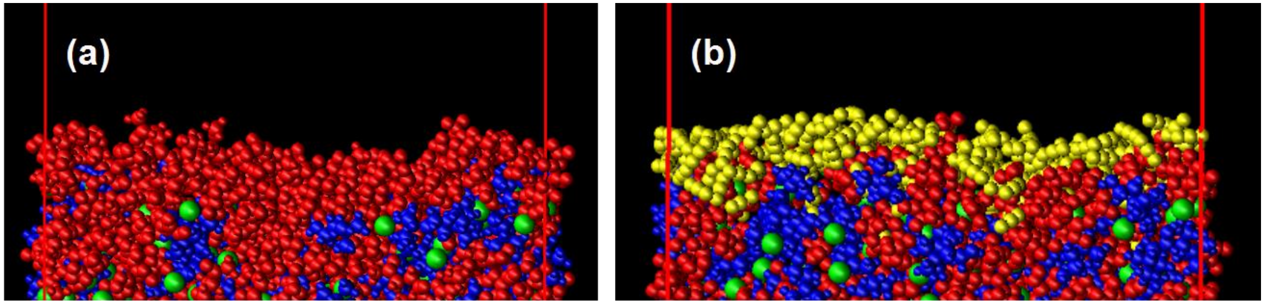
In-Situ FTIR Measurements

Other characteristics of CO_2 IR Spectra at (3600 and 3700) cm^{-1}



Further Work…

- Surface tension
- Conductivity
- NMR
- Other mixing ratios
- Molecular simulations
- [CH][Cl]+[PAC]



Snapshot of the [Ch][Cl]+LEV] 1:2
(a) vacuum or (b) CO_2 interfaces calculated from molecular dynamics simulations at 298 K. Color code: (blue) $[CH]^+$, (green) Cl^-, (red) LEV, and (yellow) CO_2. Snaphots obtained after 5.5 ns simulations.

Funding

- QNRF
  - NPRP 5-499-1-088
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- Spanish National Secretariat for Research and Development, Ministry of Economy.

الصندوق القطري لرعاية البحث العلمي
Qatar National Research Fund
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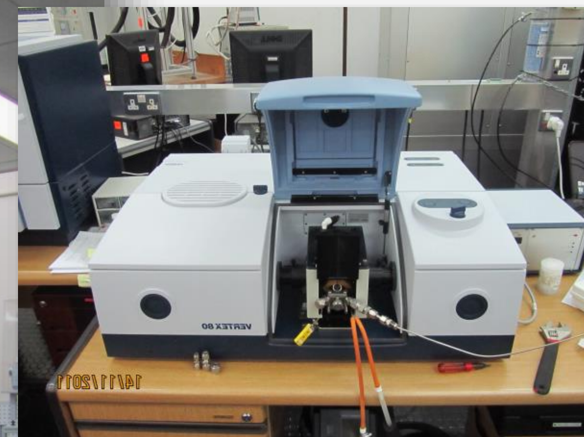
TEE Lab

Thermodynamics
Energy & Environment



Atilhan Lab, Qatar University

Group…

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TEXAS A&M UNIVERSITY at QATAR

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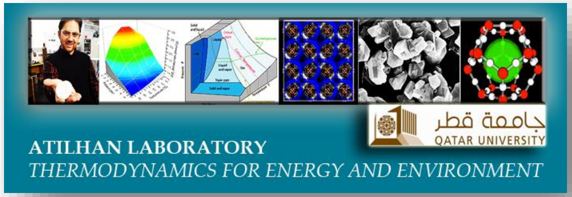

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