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Effectiveness of amino acids for carbon storage and utilization applications

Carbon dioxide (CO_2), the primary greenhouse gas, can have a major impact on global warming, if present in the earth's atmosphere beyond permissible limits. In fact, the accumulative emissions of CO_2 gas in the atmosphere are progressively increasing causing the global temperature rise by 1.5°C to 2°C (ref. 1). On the other hand, CO_2 also can form clathrate hydrates under some favourable thermodynamic conditions.

The gas hydrates (clathrate hydrates) are non-stoichiometric inclusion compounds of guest (gas) and host (cages formed from hydrogen-bonded water molecules) motifs. The gas hydrates of CO_2 molecules crystallize into a space group (Pm3n) with unit cell composition of $6L•2S•46H_2O$, where L (large) and S (small) are the cages capable of hosting guest molecules with $5^{12}6^2$ and 5^{12} faces respectively. Thus, ideally one mole of water (host) can store up to 0.174 moles of gas (guest) in the form of hydrates. In other words, the gravimetric capacity of CO_2 in hydrates is 425 mg/g. However, because of the molecular size of CO_2, it can be populated only in the large cages. Thus, the gravimetric capacity is reduced to 319 mg/g (0.130 mol/mol). On the other hand, the cage occupancy values for CO_2 gas molecules for $5^{12}6^2$ and 5^{12} cages are predicted as 0.9614 and 0.5011 respectively, using CSMGem model and thus the storage capacity is reduced to 0.147 mol (or 359 mg/g). In any case, these numbers are attractive in the perspective of carbon capture, storage and utilization (CCS&U) applications. However, the bottlenecks are slower and inefficient hydrate conversions. The common methods for increasing clathrate formation kinetics, e.g. use of high pressure (driving force), vigorous mechanical mixing, surfactants, or micron-sized ground/sieved ice particles, can be adopted in the laboratory environment. However, these may be less cost-effective and impractical in real gas-storage applications. The conversion process is quite inefficient and time-consuming in a typical batch-type reactor without an agitator and therefore, special types of reactors and/or the addition of some kinetic promoters or surfactants to the hydrate-forming (gas + water) system are often currently being used; such experiments are still at laboratory-scale.

Recently, aqueous solutions with amino acids have been demonstrated as superior thermodynamic inhibitors for both methane and CO_2 hydrates. The amino acids are attractive because of their ability to mix with water through hydrogen bonding; also, they are non-toxic and eco-friendly nature. There are 20 different essential amino acids in nature that are found in proteins. On the basis of propensity of the side chain to interact with polar solvents like water, they are classified as hydrophobic, polar or charged. In a series of papers by different researchers, it has been proved experimentally that the use of aqueous solution consisting of amino acids helps in decreasing the CO_2 hydrate formation rate, and that thermodynamic inhibition is more at higher amino acid concentration[2]. Most of these experiments were conducted under stirred conditions to form CO_2 hydrates[2]. The inhibition effect has been correlated with hydrophobicity, length and constituents of the side chain, and concentration in aqueous water. But there is no thorough agreement among various experiments conducted by different groups and thus the underlined mechanism is more obscure. On the other hand, Cai *et al.*[3] reported that some amino acids like L-methionine, L-norvaline and L-norleucine have a large CO_2 gas storage potential in the form of hydrates and with faster gas uptake, even under non-stirred configuration. Thus, some amino acids could be a useful material for CCS&U applications. The present study aims at assessing the CO_2 gas storage capacity in four different amino acids, mostly found in proteins, namely L-valine (l-val), L-phenylalanine (l-phe), L-cystein (l-cys) and L-methionine (l-met) in isochroic and non-stirred conditions. The chosen amino acids have significant variations in parameters such as hydrophobicity, length and type of the side chains.

Figure 1 describes the experimental procedure adopted and is self-explanatory. The experimental procedure and data analysis are similar to our earlier studies[4,5]. Briefly, the solution was introduced in

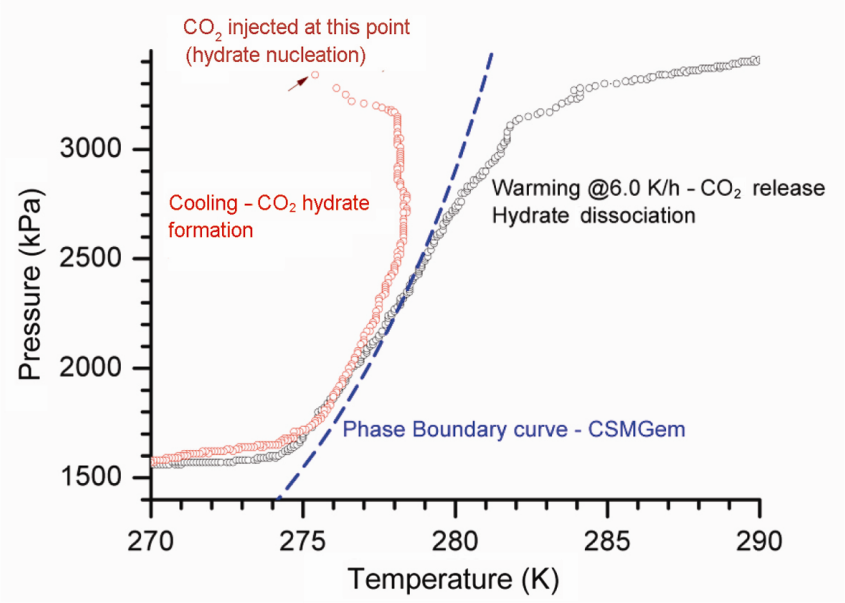

Figure 1. Pressure–temperature trajectory for 0.5 wt% l-met + H_2O + CO_2 system.

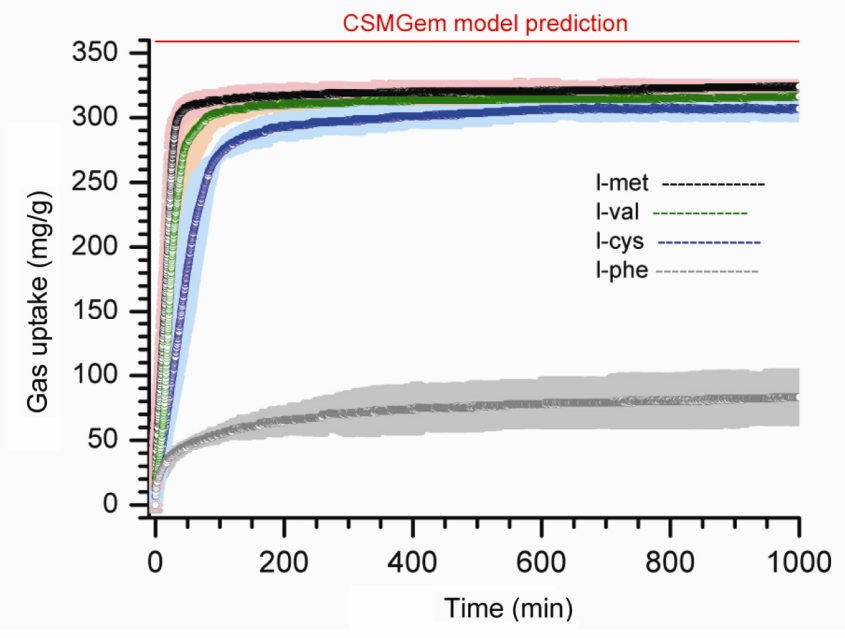

Figure 2. CO_2 gas uptake kinetics for various amino acids (0.5 wt%) + H_2O + CO_2 system during hydrate formation. CO_2 gas was injected into the reactor vessel at 273 K.

the reactor vessel and cooled to about 273 K, then CO_2 gas was quickly injected. The process of hydrate nucleation and subsequent growth is exothermic in nature. Thus, there will be heat release, causing an increase in local temperature. The temperature was increased to ~277 K, and there was a significant decrease in the reactor pressure indicating hydrate nucleation and growth. The system was held under these conditions for more than 12 h and then the temperature was lowered again to about 268 K. Noticeably, the pressure drop was marginal, indicating the completion of hydrate conversion. Thereafter, the temperature was rapidly increased (@ 6 K/h) to 298 K. The significant release of CO_2 gas occurred in the temperature range 274–283 K and the path was along the phase boundary curve predicted by CSMGem.

Cai *et al.*[3] have reported aqueous solution with l-met as an effective promoter for CO_2 hydrates; the efficiency depends on the amount of l-met. The optimal performance was observed for 0.2 wt% l-met with gravimetric capacity as 356 mg/g and t_{90} (time taken for 90% of gas consumption) was only about 15 min. Upon increasing l-met concentration to 0.5 and 1.0 wt%, the gravimetric capacity was reduced to 346 and 321 mg/g respectively. Noticeably, there was no change in the gas uptake kinetics. On the other hand, for lesser l-met concentration, i.e. 0.02 and 0.05 wt%, the gas storage capacity was 350 mg/g, while t_{90} was slightly longer[3]. As shown in Figure 2, our experimental value is 324 mg/g for the same system, i.e. 0.5 wt% l-met. The shaded part in this figure represents the error from repeat measurements. Interestingly, the storage capacity for 0.5 wt% l-met solution is 90% of the CSMGem model predicted value. Also t_{90} in our experiments is 30 min, which is twice longer than the reported value[3]. As mentioned earlier, the phase transformation to hydrate is an exothermic change, associated with heat release. It is possible to reduce t_{90} and further increase the gas storage capacity by improving heat and mass transfer efficiency of the process.

We conducted experiments under similar conditions using l-cys, l-val and l-phe. As shown in Figure 2, the gas storage capacity in l-cys and l-val systems is 306 and 315 mg/g respectively. The t_{90} for these systems, is 110 and 52 min respectively. On the other hand, gas consumption is significantly less in l-phe system (83 mg/g and $t_{90} > 400$ min). Cai *et al.*[3] have also examined gas storage capacity using 0.2 wt% L-norleucine (l-nle) and L-norvaline (l-nva) and found it to be 362 mg/g ($t_{90} = 28$ min) and 361 mg/g ($t_{90} = 400$ min) respectively. L-norleucine is isosteric to l-met and does not possess sulphur atom in the side chain. Both of them are good promoters for CO_2 hydrates. Similarly, l-met and l-cys having 'sulphur' atom in the side chain also show the promotion effect (Figure 2). On the other hand, l-phe which has similar hydrophobicity as other amino acids, shows feeble promotion effect for CO_2 hydrates.

All these factors indicate that the hydrate promotion effect has no simple correlation with the hydrophobicity or nature of the amino acid side chain. Therefore, the exact mechanism of hydrate promotion at this stage remains obscure. Nevertheless, certain amino acids, such as l-met, l-cys, l-nle, l-val, l-nva, etc. have been proved to be good promoters for CO_2 hydrate formation. The faster gas uptake kinetics and effective hydrate conversion at favourable thermodynamic conditions could be utilized for CO_2 gas storage applications.

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Low phytic acid peanut: a potential tool to overcome mineral malnutrition in humans

Malnutrition affects over one billion people worldwide and thus one out of six humans is malnourished. Though the green revolution solved the problem of malnutrition to the great extent, people living in developing and under-developed countries still face micronutrient malnutrition, which is a result of imbalanced diet and intake of insufficient micronutrients. Iron and zinc deficiencies together contributing to loss to GDP is at least US$ 5 billion in China and India alone[1].

Among nuts, peanut is considered as superfood and has been effective in treating malnutrition across the globe. Peanuts have more protein and 30 essential vitamins and minerals that are effective to combat acute malnutrition. Nutritive value of peanuts reveals that nearly half of the mass of the kernel is made of lipids, whereas protein and carbohydrate constitute nearly one-fifth to one-fourth of the kernel mass. The total mineral content of peanuts is in the range 2–3% and is a good source of iron, potassium, calcium, sodium and magnesium. It also contains appreciable amounts of manganese, copper, zinc and boron[2]. Peanut kernels contain more protein than meat and egg, and far more than any other vegetable foods, except soybean. The National Aeronautical and Space Administration, USA, has selected peanut as food for advance life-support systems for extended space missions[2].

In addition to the huge beneficial properties, peanuts also have very high levels of phytic acid than wheat, maize and barley and lower inorganic phosphorus content than pigeon pea, chickpea, urdbean and soybean[3]. Phytic acid content is 0.2–4% in peanuts and a huge variability among peanut genotypes with respect to phytic acid content has been observed (812.3–1713.8 mg/100 g seed)[4]. Phytate is a chelator of cations such as Fe^{2+}, Zn^{2+}, Ca^{2+} and Mg^{2+}, and reduces their bioavailability in humans and monogastric animals[5]. In developing countries where staple food is mainly seed-based, it leads to serious alimentary deficiencies in humans[3]. Non-ruminant animals are unable to digest phytic acid, and the undigested phytic acid promotes water eutrophication and environmental pollution[6]. This warrants the development of low phytic acid crops[7].

Phytic acid in plants is synthesized either by lipid-dependent pathway or by lipid-independent pathway, which begins with glucose 6-phosphate (G6P) (1) and 1D-myo-inositol 3-phosphate synthase (MIPS) catalysing this step. In lipid-dependent pathway, inositol gets converted into phosphatidylinositol (PtdIns) and is later phosphorylated to yield PtdIns(4,5)P_2, subsequently being hydrolysed via the action of a specific phospholipase C to yield Ins(1,4,5)P_3 and finally phytic acid. In lipid-independent pathway, inositol is sequentially phosphorylated to di-, tri-, tetra-, penta phosphates and finally to phytic acid[8].

A reduction in phytic acid content and increase in P content in seeds is desirable as it reduces the environmental impact due to animal waste. Efforts to reduce phytic acid mainly involve three approaches: (1) expression of recombinant microbial phytase; (2) generating low phytic acid mutant phenotypes through mutation – several such mutants have been identified in rice[9], wheat[10], maize[11], soybean[12] and other crops; (3) generating transgenic lines by suppressing genes involved in phytic acid biosynthesis. An advantage of the third approach is that genetic manipulations can be carried out in a developmentally and physiologically regulated system[13], which is otherwise lacking in the mutagenic approach.

Unlike cereals, molecular breeding or genomic assisted breeding efforts are limited in peanut. When compared to other genomic resources, molecular markers can be directly applied in crop breeding and for marker-assisted breeding to be utilized in developing low phytic acid genotypes, genes/quantitative trait loci (QTLs) involved in this pathway have to be identified[14]. At present, several genomic resources like expressed sequenced tags (ESTs), physical maps, molecular markers, QTL identification and identification of genes associated with the traits of interest are available. Recently, *AhPIPK1*, one of the genes involved in lipid-dependent phytic acid biosynthetic pathway[15], and *AhIPK2* and *AhITPK1* involved in lipid-independent phytic acid biosynthetic pathway[16] have been identified in peanuts. This opens up new avenues for practising genomic-assisted breeding for reducing phytic acid content in peanuts. Low phytic acid genotypes of maize, barley and soybean