Solubility Measurement and Modelling of Urea in Supercritical CO_2 and CO_2 + Ethanol Mixtures

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The solubility of urea in supercritical CO_2 and CO_2 + ethanol was measured over the pressure and temperature ranges 100 – 300 bar and 313 – 373 K respectively, and ethanol concentrations 0 – 25 % by mass (urea free basis). The solubility in CO_2 was measured by a once-through packed bed gravimetric method at a laboratory and pilot scale. The solubility in CO_2 + ethanol was measured using two different gravimetric methods: antisolvent precipitation and gravimetric packed bed. The solubility of urea in pure CO_2 is very low, ranging from 1.1×10^{-6} mole fraction at 100 bar, 333 K to 3.1×10^{-5} at 300 bar, 353 K. The solubility increases exponentially with a linear increase in ethanol content. The highest solubility measured was ~ 1×10^{-2} mole fraction at 333 K, 150 bar and 26 % ethanol. At high ethanol contents, the solubility was almost independent of pressure at a fixed temperature. The solubility was correlated by the Peng-Robinson equation of state with various mixing rules for the repulsive and attractive parameters. It was not possible to find pairs of interaction parameters that modelled both the solubility in pure CO_2; and CO_2 + ethanol. The solubility of urea in ethanol, and ethanol in CO_2 was also modelled to obtain interaction parameters for the model. Ethanol appears to increase the solubility above that predicted using interaction parameters derived from urea/pure CO_2 and ethanol/CO_2 binaries. This increase in solubility may be due to favourable interactions between ethanol and urea, such as hydrogen bonding.

INTRODUCTION

Urea is a widely used agrochemical that is highly water soluble, and poorly soluble in non-polar organic solvents. The solubility of urea in supercritical CO_2 and CO_2 + ethanol does not appear to have been measured before by other groups, although it has been used as a model compound for antisolvent precipitation [1] using CO_2; for the in situ urea complexing of fatty acid esters [2]; and extraction of fatty acid esters from urea [3] using CO_2. Recent studies have shown that polar compounds with suitable functional groups are capable of forming dimers in solution, and/or forming complexes with alcohol co-solvents in CO_2 [4,5]. Urea is expected to have low solubility in supercritical CO_2, but to be able to form hydrogen bonded complexes with ethanol as a co-solvent due to the hydrogen bond acceptor carbonyl group, and hydrogen bond donator amine groups. In this work, the solubility of urea is measured in pure CO_2 by a packed bed continuous flow method; and in CO_2 + ethanol by packed bed and antisolvent precipitation methods. The solubility of urea in CO_2 and CO_2 + ethanol was modelled using the Peng-Robinson equation of state [6]

EXPERIMENTAL

Urea was obtained from Ravensdown NZ Ltd. Absolute ethanol was obtained from Scharlau. Carbon dioxide was obtained from BOC (NZ) Ltd. The solubility of urea was measured in a laboratory scale plant shown in figure 1. A packed bed of urea of known mass was placed into the 500ml extraction vessel EXV1. The extraction apparatus was pressurised to the operating pressure using air-driven compressor DC1. CO_2 then passed downwards through the packed bed contained within extraction vessel EXV1, before passing through a back-pressure regulator PRV1, and into separation vessel SV1. The CO_2, now gaseous, passed through coriolis flow meter FM1 and water trap WT1, where it was mixed with make-up liquid CO_2 from cylinder OC1. The liquefied mixture passed through sub-cooler heat exchangers HE1 before being recycled back to DC1. After a sufficient mass of CO_2 had passed through the packed bed to ensure a measurable amount of urea was extracted, the experiment was stopped and EXV1 vented, initially back to the cylinders and then to atmosphere. The packed bed was weighed, stored in a sealed vessel overnight, and then reweighed. The urea collected in separation vessel SV1 was removed with the aid of ethanol, which was forced through the extraction vessel (after the bed had been removed), connecting pipework, and valve PRV1. The mass loss of the bed was compared with the mass recovered after evaporation of ethanol to determine the mass balance, and solubility. The experiments were carried out over long time periods and high circulation rates to minimise the weighing errors associated with the measurement of lowly-soluble materials.

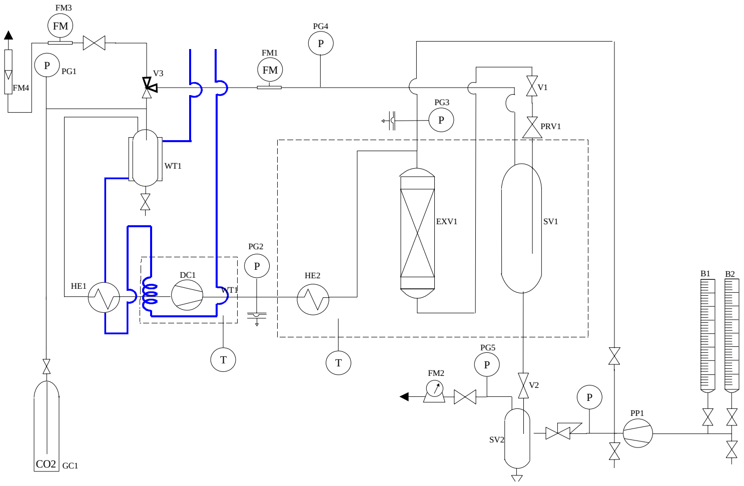

Figure 1 Schematic of solubility apparatus

When ethanol was used as a co-solvent, the apparatus was used in a once-through flow mode. When the extraction vessel was pressurized as above, ethanol pump PP1 was started at the same time as flow began through the packed bed. Samples of urea dissolved in ethanol were recovered from the separator SV1 at regular time intervals, and the ethanol removed under vacuum to obtain the solubility. The separator was operated at a pressures of 20 - 40 bar, to maximise the recovery of ethanol. Again, the mass collected in the separator was compared with the mass loss from the bed (after heating to remove any residual ethanol) for mass balance purposes. Antisolvent experiments were performed by modifying the apparatus to enable the CO_2 and ethanol/urea mixture to contact each other inside the extraction vessel. Ethanol solutions containing a known concentration of urea were pumped into the extraction vessel using PP1 through the inside pipe of a concentric pipe arrangement. CO_2 passed through the outer pipe, and contacting took place at the outlet of the ethanol/urea pipe. Precipitated urea was collected in the extraction basket, which was heated and weighed at the end of the experiment. Ethanol and non-precipitated urea that was recovered in the separator SV1 were separated under vacuum to enable a mass balance to be performed. The apparatus was further modified for low ethanol packed bed solubility measurements. A second pump (not shown in figure 1) was added. This pump injected ethanol into the CO_2 after the extraction bed and before PRV1 to ensure complete collection of urea.

MODELLING

The Peng-Robinson equation of state with two interaction parameters was used to model the phase equilibrium. The equations for the solubility of a solid in a near-critical fluid have been presented in detail elsewhere [7]: here the mixing rules are presented for completeness.

$$a_m = \sum_{i=1}^{n}\sum_{j=1}^{n} a_i^{0.5} a_j^{0.5} (1 - k_{ij})$$

$$b_m = \sum_{i=1}^{n}\sum_{j=1}^{n} b_1^{0.5} b_j^{0.5} (1 - l_{ij})$$

The model requires interaction parameters, k_{ij} and l_{ij}, for the binary systems CO_2/ethanol; CO_2/urea; and ethanol/urea. The Peng-Robinson equation was also used to obtain these parameters by obtaining a best fit between literature data for CO_2/ethanol [8,9] and ethanol/urea [10,11]; and the data obtained in this work for CO_2/urea. The sublimation pressure of urea was obtained from [10]. Urea critical parameters were estimated using the Joback group contribution method [12]

RESULTS AND DISCUSSION

I – SOLUBILITY OF UREA IN SUPERCRITICAL CO_2

The solubility of urea in pure supercritical CO_2 was measured in the apparatus shown in figure 1 using recycle of solvent. The solubility of urea in CO_2 was very low, reaching a maximum mole fraction of 3 × 10^{-5} at 353 K and 300 bar. The solubility was highly temperature dependent, which reflects the relatively high vapour pressure of the solid. At low pressures, the solubility was not highly dependent on pressure, whereas at high temperature, the solubility showed some pressure dependence. The solubility in pure CO_2 is shown in figure 2. The Peng-Robinson EOS with interaction parameters, k_{ij} = 0.095 and l_{ij} = -0.2571, was able to fit the data well.

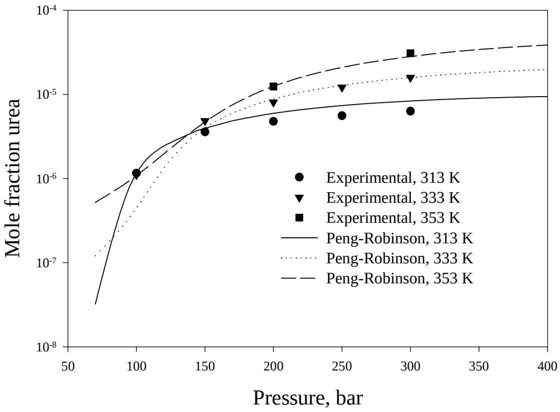

Figure 2 Solubility of urea in CO_2

II – SOLUBILITY OF UREA IN SUPERCRITICAL CO_2 + ETHANOL

The solubility in CO_2 + ethanol showed completely different behaviour to the solubility in pure CO_2. The solubility increased exponentially with ethanol at fixed temperature

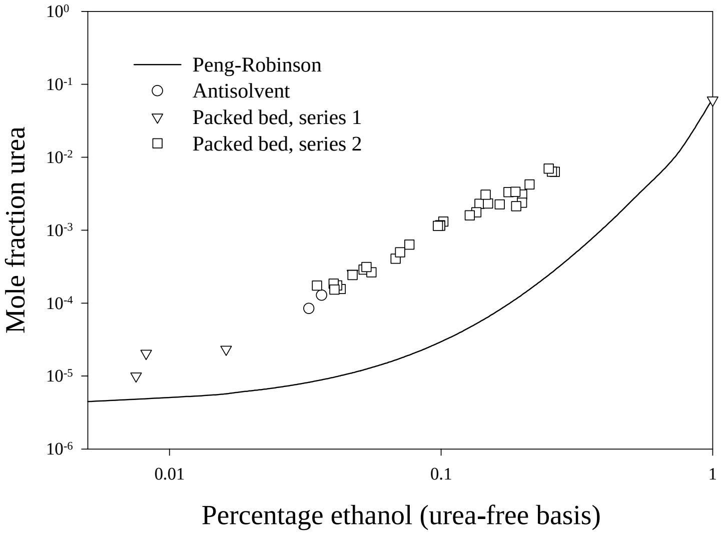

Figure 3 Solubility of urea in CO_2 + ethanol at 313 K and 150 bar

and pressure. The solubility results for 150 bar, 313 K are shown for fixed bed and antisolvent-type measurements, over a broad range of ethanol concentrations in figure 3. The solubility of urea in pure ethanol at 150 bar and 313 K is also shown, along with the predicted solubilities using the Peng-Robinson equation of state with interaction parameters from CO_2/ethanol, CO_2/urea and ethanol/urea binary systems. There is good agreement between the experimental methods, but poor agreement with the EOS, except at the extremes of the ranges, i.e. at zero percent ethanol (not shown on the graph) and 100 % ethanol. There is some scatter in the data at low ethanol concentrations, due to the difficulties in performing the experiments.

The solubility of urea in CO_2 + ethanol is shown at 150 bar, 313 and 333 K; and 300 bar, 313 and 333 K in figure 4. There is some scatter in the data at high ethanol concentrations – however, there is no discernable pressure dependence, and very little temperature dependence. This is an unusual finding, as there is pressure dependence in the solubility of urea in pure CO_2. The solubility of most solids measured in CO_2 + co-solvent show some pressure dependency. At 100 % ethanol, there is temperature dependence in the data, which matches the temperature dependence of solubility at atmospheric pressure [10,11]. The Peng-Robinson EOS predicts that there is a slight decrease in solubility of urea in pure ethanol as the pressure is increased. This prediction is observed in the experimental measurements.

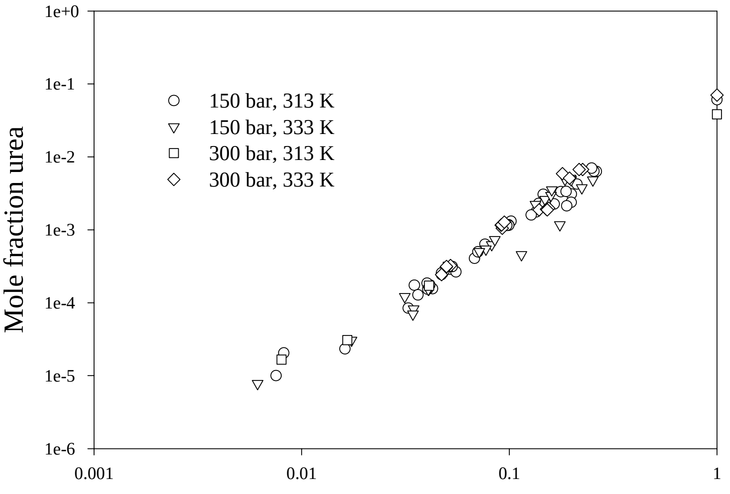

Figure 4 Solubility of urea in CO2 + ethanol at 313 - 333 K and pressures of 150 and 300 bar

III – MODELLING OF THE SOLUBILITY OF UREA IN CO2 + ETHANOL

Interaction parameters derived from binary systems could not model the solubility when using the Peng-Robinson equation of state. The fit of the model is highly dependent on the interaction parameter between CO_2 and urea. The best-fit interaction parameter when fitted against the CO_2 + ethanol experimental data was substantially larger than that obtained from the binary system, suggesting that there is a much stronger interaction than that obtained from dispersion forces alone. Hydrogen bonding interactions have been determined experimentally for ethanol and other n-alcohols in supercritical CO_2 [13]. There have been a number of reports showing that hydrogen bonding occurs between ethanol (as a co-solvent) and solutes that have hydrogen donor and/or acceptor capabilities, such as fatty acids [4,5]. Additionally, the solutes are able to exist as dimers, even at very low co-solvent concentrations [4,5]. We are unable to determine from our experiments whether hydrogen bonding and dimerization occurs. However, the structure of urea suggests that hydrogen bonding should be possible when ethanol is present as a co-solvent. Hydrogen bonding would be minimal or non-existent for pure CO_2, giving rise to a low interaction parameter for the attractive term in the Peng Robinson EOS. However, in pure ethanol, it is likely that urea forms strong interactions, and that interaction parameters determined from solubility data are for urea complexes in ethanol. The Peng-Robinson EOS gives a surprisingly good fit to the literature data at atmospheric pressure, and high pressure data measured in this work. A parity plot is shown in figure 5. The fit of the EOS diminishes with increasing temperature. It is known that the strength of hydrogen bonds also diminishes with temperature. In future work, we intend to model the solubility assuming that complex formation has occurred, according of the models of Lemert and Johnston [14] and Ting et al [15].

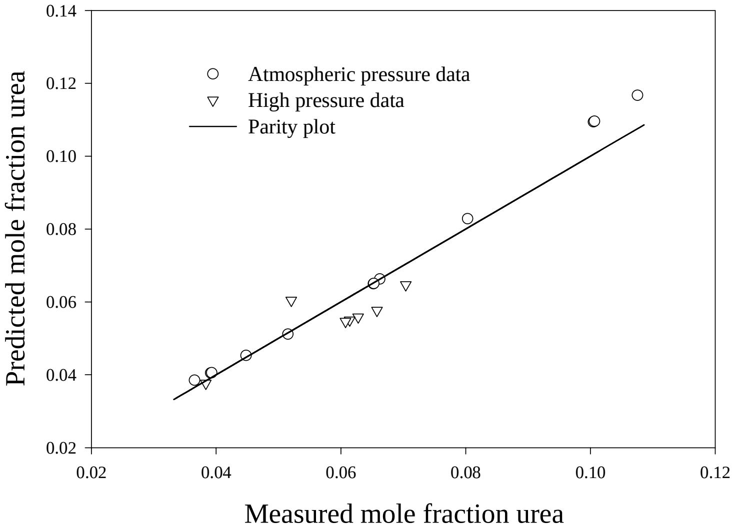

Figure 5 Parity plot of predicted versus measured solubility of urea in ethanol at atmospheric and high pressure (150 and 300 bar)

CONCLUSIONS

The solubility of urea was measured in pure CO_2, CO_2 + ethanol, and pure ethanol at pressures in the range 100-300 bar, and temperatures of 313 – 353 K. The solubility of urea in pure CO_2 was low, and followed solubility behaviour normally observed in supercritical fluids. The solubility in CO_2 + ethanol was highly dependent on the ethanol concentration in the supercritical fluid mixture, and weakly dependent on pressure and temperature within the ranges investigated. At ethanol mole fractions in the range .01 - .25, there was no pressure and temperature dependence. It is postulated that the lack of influence of temperature and pressure is due to strong interactions between the co-solvent, ethanol, and urea. The Peng-Robinson EOS was able to model the solubility of urea in pure CO_2 and in pure ethanol, but not in the mixture when using interaction parameters derived from the relevant binary systems. Further work is required to improve the fit of the model by incorporating interaction parameters to account for the formation of complexes between urea and ethanol; and dimers of urea.

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