Measurement and modeling of the solubility of phosphatidylcholine in dimethylether and water

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Introduction

Subcritical dimethylether (DME) is a solvent that is compatible with food processing applications and has a relatively high mutual solubility with water, which makes the extraction of solids from an aqueous stream theoretically possible. This paper describes measurements and modeling of liquid-liquid equilibria between DME and water, and between water, DME, and a model polar lipid fraction consisting predominantly of phosphatidylcholine.

Experimental

The lipid fraction used in this work was extracted from spray dried egg yolk powder by first using supercritical CO_2 to remove neutral lipids from the powder and then using dimethylether (DME) to extract a predominantly polar lipid fraction. HPLC analysis of the resulting extract showed a composition by mass of 67% phosphatidylcholine, 23% phophatidylethanolamine, 4% phosphatidylinositol, and less than 5% neutral lipid. Some measurements were also conducted with a commercially available soy lecithin.

Equilibrium phase concentrations were measured by contacting the DME, water, and lipid in a counter-current flow column, indicated in Fig 1. Dimethylether (DME) was pumped into the bottom of the column and contacted with an aqueous feed stream introduced at the top of the column. Extract and DME from the top of the column was taken off continuously through a pressure reduction valve into a heated separator. DME from the separator was recycled through a flow meter and condenser. The raffinate phase was withdrawn periodically from the bottom of the column through a pressure reduction valve. A sight glass was used to observe the phase interface and maintain a liquid level at the bottom of the column. DME separated from the raffinate phase was vented through a flow meter.

All flow rates were measured, so that the composition of the raffinate phase and the extract phase from the column could be calculated. Allowance was made for the DME retained in the extract and raffinate, and for water vapour carried over in the DME vapour phases, by assuming equilibrium conditions existed in the separators and using vapour-liquid equilibrium data by Pozo and Street [1]

Water solubility measurements were made for pressures from 8.5 bar to 40 bar at 292 K and from 10 bar to 100 bar at 324 K. For measurements including the lipid fraction, measurements were mainly at 40 bar. Feed concentrations of up to 5% lipid by mass were used. This quantity of lipid was totally soluble in DME, so that for equilibrium conditions in the column the measurements represent a phase boundary in which the DME phase is water saturated. Measurements were also conducted in which a 40:60 by mass mixture of lipid and water was extracted by passing DME through. This measurement (ideally) gives a limiting solubility for both lipid and water.
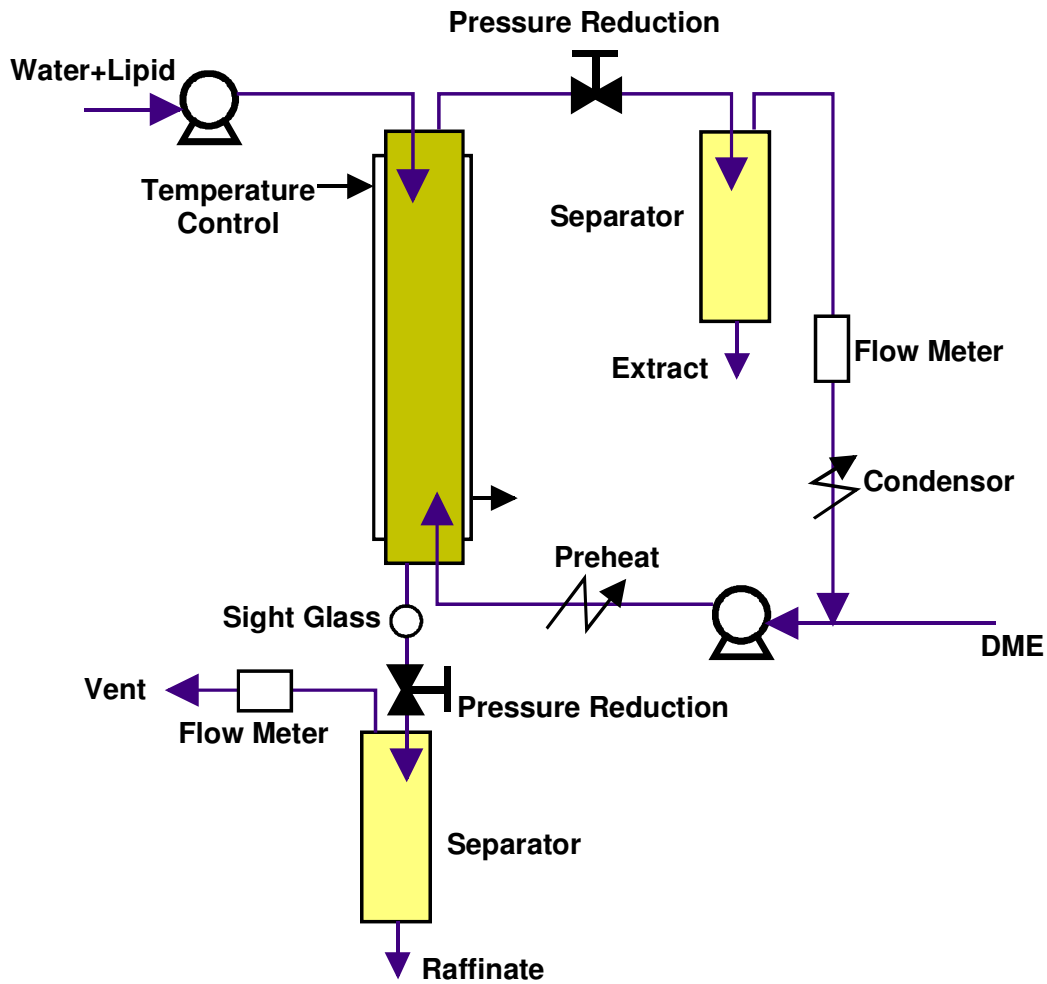
Figure 1 – Schematic of antisolvent fractionation apparatus used for phase equilibrium measurements

Measurements using soy lecithin were made using a 'once through' method. DME, with and without water premixed as a co-solvent, was passed through a packed bed of lecithin granules. The lecithin was recovered from the DME and water to determine the fraction of lipid in the extract phase.

Modeling

Phase equilibria were modeled using the Peng Robinson equation of state. The approach followed is consistent with that described, for example, by Smith et al [2] for calculation of liquid-liquid and liquid-vapour equilibria. Details of this method are not repeated here, but for completeness the mixing rule used is given by Equations 1,2. Critical parameters for water and DME used in the model were obtained from Poling et al [3].

$$a_{mix} = \sum_i \sum_j \sqrt{a_i a_j}\,(1 - k_{ij})\,y_i\,y_j, \quad with\ k_{ii} = 0 \tag{1}$$

$$b_{mix} = \sum_i \sum_j \frac{(b_i + b_j)}{2}(1 - l_{ij})y_i y_j, \quad with \ l_{ii} = 0 \qquad (2)$$

The temperature dependent parameters k,l were calculated by minimising the sum of the squared error between measured and predicted values. Data by Pozo and Streett [1] for liquid-liquid and liquid-vapour equilibria were included with experimental measurements made here.

DME / Water phase equilibria

Experimental and modeling results for the water/DME system are shown in Figure 2. The solubility of DME in the water phase ranges from 15% to 20% (mole fraction) over the range of liquid/liquid equilibria conditions examined in this work. The solubility of water in the DME rich phase ranged from 19% to 25%. Also plotted are liquid-liquid equilibria measurements reported by Pozo and Streett [1] at 373K and vapour-liquid equilibria measurements at 323K and 373K. The solubility of water in DME increased with an increase in
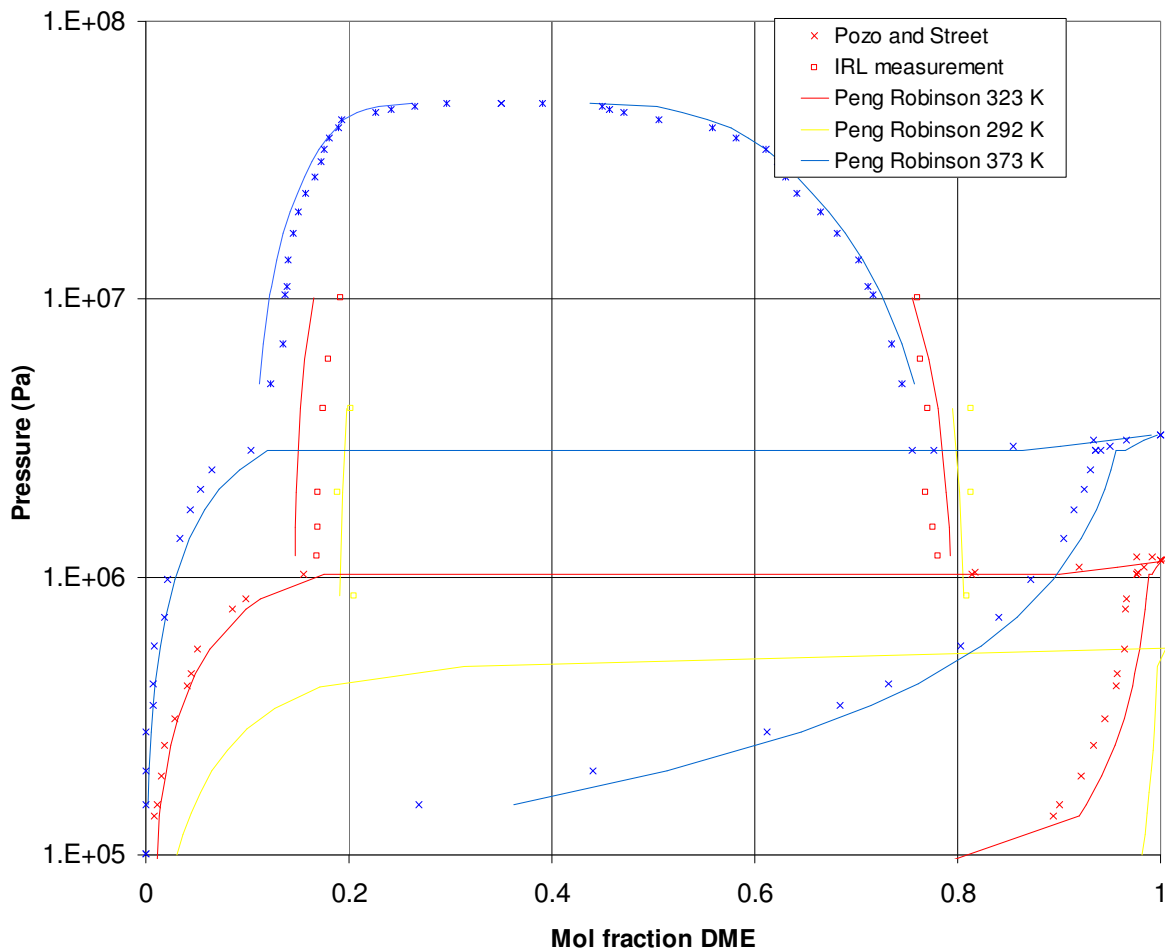
Figure 2 – Modeling of DME/Water system and comparison with data of Pozo and Streett [2] and data from this work. Parameter _k_ is -.361+0.00085T. Parameter _l_ is 0.124-0.00005T (T in Kelvin).

temperature, whereas the solubility of DME in the water rich phase decreased with increasing temperature. There was very little change in solubility with pressure, except near the liquid/vapour transition (the lowest pressures measured in this work).

The Peng-Robinson equation of state was fitted to this data with a value for *k* of -0.361+0.00085T, and for *l* of 0.124-0.00005T (T in Kelvin). There is good agreement between theory and experimental results, including the small region where two liquid phases are in equilibrium with a DME vapour phase.

DME / Water / Lipid phase equilibria

The composition of the raffinate and extract phases in the system DME/Water/Lipid is shown in Figure 3 for a pressure of 40 bar and a temperature of 313K. Limited results are also shown for measurements at 333K.

The results show an increase in water solubility with increasing mass fraction of lipid in the DME phase, suggesting a positive interaction between the water and lipid to increase their mutual solubility in DME. A single measurement at 333K shows no significant change in water solubility with temperature beyond the degree of uncertainty in the data. This is in contrast to a noticeable temperature dependency in the binary water/DME system.

The raffinate phase (water rich right hand side of Figure 3) shows a degree of scatter, mostly associated with uncertainty in measurement of the DME fraction contained in the
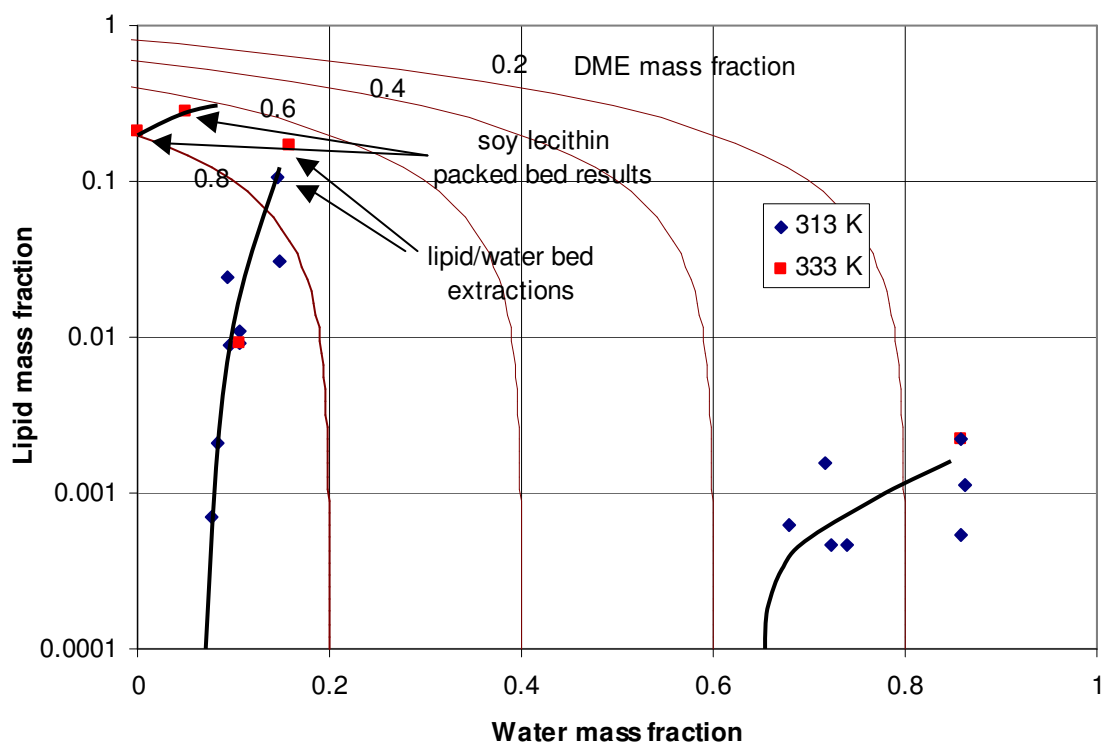
Figure 3 – Phase boundaries for polar egg yolk lipid in water saturated DME. Solid lines are not model predictions. Measurements are at 40 bar.

raffinate – good separation of the two phases was difficult and some additional DME is expected to have been entrained in the raffinate in some cases. There is a suggestion of an interaction between the DME solubility in the water phase and lipid content but this is difficult to determine. There is again no significant indication of a dependence on temperature.

Measurements made by extraction of lipid and water from a solution of 40:60 lipid/water by mass are also shown in Figure 3 (labelled as lipid/water bed extractions). These results (ideally) represent the saturation point for both lipid and water in DME. There was some indication in the results that a steady state condition may not have been reached, so the true limiting solubilities for the lipid in DME and water may be higher than recorded here. Soy lecithin packed bed results show a 21% mass fraction of lipid in DME, increasing to 28% with 5% water co-solvent.

Summary

Water/DME, and water/DME/lipid liquid-liquid equilibria were measured in a counter-current flow column. Results for the water/DME system show good agreement between model and experiment, including prediction of gas-liquid solubilities at lower pressures reported by other authors. A small region where two separate DME/water liquid phases co-exist was also well modeled.

Water/DME/lipid measurements indicate an increase in water solubility in DME with an increasing lipid content. There was little effect of temperature on the water solubility in the presence of lipid, but a significant increase in solubility with temperature for the binary water/DME system. The effect of pressure on DME/water mutual solubility was minimal.

References

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2. Smith, J.M., Van Ness, H.C., Abbott, M.M., Chemical Engineering Thermodynamics, Sixth Edition, McGraw Hill, 2001
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