Solubilities of Substituted Phenols in Supercritical Fluid Carbon Dioxide

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Introduction

In recent years, there has been increased interest in supercritical fluid (SCF) technology. SCF extractions/separations are an attractive alternative to vacuum distillation or liquid extraction processes. The unique properties of supercritical fluids (SCF) that make them attractive for separation processes depend on the fluid density, which can be adjusted by controlling the temperature and pressure. Carbon Dioxide (CO₂) is a commonly used supercritical fluid due to its low cost and its relative nontoxicity. It has found industrial and analytical applications in the environmental and food industries.

Binary Solubility

Recent studies on polar multicomponent systems indicate solubility enhancements, which could be associated with strong solute-solute interactions such as hydrogen bonding. Solubility enhancements usually follow a parabolic solubility relationship in the form of a second-order polynomial equation, which can be used to predict the solubility of a solute in a mixed solvent system.

It has been observed that in mixed solute systems, the solubility of the components in SCFs may be considerably different from their respective binary solubilities. Binary solubilities of substituted phenols ranged from 10⁻⁵ to 10⁻² mole fraction and varied in the following order.

1. 2,5-Dimethylphenol (2,5-DMP)
2. 2,4,6-Trimethylphenol (2,4,6-TMP)
3. 2,3,5-Trimethylphenol (2,3,5-TMP)
4. 4-Phenylphenol (4-PP)
5. 4-Tert-butylphenol (4-tBuP)

Solubility data for the compounds of interest is essential for the design of any SCF-based process. Technical difficulties encountered in mixed-solute separation include solvent selection, breakthrough behavior, and product purity. The phase behavior of organic solids in CO₂ can be quite complex. Pure solvents, such as liquid CO₂, may be more significant in mixed solute systems.

Results and Discussion

Table: Binary Solubilities of Substituted Phenols in SCF CO₂ (Mole Fraction)

<table>
<thead>
<tr>
<th>Phenol</th>
<th>101 bar</th>
<th>152 bar</th>
<th>203 bar</th>
<th>254 bar</th>
<th>285 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-DMP</td>
<td>0.001</td>
<td>0.004</td>
<td>0.008</td>
<td>0.012</td>
<td>0.016</td>
</tr>
<tr>
<td>2,4,6-TMP</td>
<td>0.002</td>
<td>0.008</td>
<td>0.016</td>
<td>0.024</td>
<td>0.032</td>
</tr>
<tr>
<td>2,3,5-TMP</td>
<td>0.003</td>
<td>0.013</td>
<td>0.026</td>
<td>0.040</td>
<td>0.053</td>
</tr>
<tr>
<td>4-PP</td>
<td>0.005</td>
<td>0.020</td>
<td>0.040</td>
<td>0.060</td>
<td>0.080</td>
</tr>
<tr>
<td>4-tBuP</td>
<td>0.007</td>
<td>0.032</td>
<td>0.064</td>
<td>0.096</td>
<td>0.128</td>
</tr>
</tbody>
</table>

Experimental Method

A schematic diagram of the apparatus is shown in Figure 1. The apparatus was designed and constructed at MTU in the Spring of 2000. A novel sample introduction technique was developed to reduce sample introduction errors. Light scattering was used to obtain the concentrations of the solutes.

The phase behavior of organic solutes in CO₂ can be split into three regions: pressurized, normal, and pressurized normal. Pressurized solvents, such as liquid CO₂, may be more significant in mixed solute systems. Technical difficulties encountered in mixed-solute separation include solvent selection, breakthrough behavior, and product purity.

Phase Behavior

The phase behavior of organic solutes in CO₂ can be split into three regions: pressurized, normal, and pressurized normal. Pressurized solvents, such as liquid CO₂, may be more significant in mixed solute systems. Technical difficulties encountered in mixed-solute separation include solvent selection, breakthrough behavior, and product purity.

References

1. Ravipaty, S.; Chesney, D. J. Presented at the Pittsburgh Conference, New Orleans, LA, March 2001; paper 1753P.