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SOLUBILITIES OF COMPLEX LIQUID MIXTURES
IN DENSE GASES

Agustine Monge and John M. Prausnitz

August 1982
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An Experimental Technique for Determining Solubilities of Complex Liquid Mixtures in Dense Gases

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ABSTRACT

A flow method has been developed for measuring solubilities of heavy complex mixtures in compressed gases to 100 bar and 600 K. Quantitative analysis of the effluent gas is not required; therefore, this method is suitable for liquid mixtures containing many unidentified components. Further, the method is suitable for gaseous mixtures containing a subcritical component such as water.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.
For high-pressure process design (e.g. supercritical-fluid extraction), it is often necessary to know the solubility of a heavy-component mixture in a compressed gas. Experimental methods for measuring such solubilities have been reported by numerous authors, including, for example, Diepen and Scheffer (1948), Rigby and Prausnitz (1968), Czurbryt et al. (1970), Simnick et al. (1977), Kaul and Prausnitz (1978), McHugh and Paulaitis (1980), Kurnik and Reid (1982) and Johnston and Eckert (1981). These methods require gravimetric measurements or chemical analysis (usually by gas-liquid chromatography) for the heavy component. Since nearly all experimental work in this area has been confined to systems wherein all components (usually only two) are clearly identified, chemical analysis is straightforward. However, if the heavy liquid is a mixture of many unidentified components (e.g. a narrow-boiling fraction from a heavy-fuel source), such analysis may be difficult, perhaps impossible. For such mixtures, gravimetric analysis is also not useful because, when volatility is low, an excessive amount of time is required to complete one run. Therefore, we have developed an experimental solubility method which can be completed in a reasonable time frame and does not require quantitative chemical analysis.

Experimental methods which replace precise, quantitative, chemical analysis with gravimetric measurement
are essentially restricted to noncondensible gases; they are not useful for gas mixtures containing a subcritical gas as, for example, water vapor. Our technique, however, has been used to measure the solubility of a heavy fraction in a compressed methane/water mixture. This capability is important because water is often present in processing heavy fossil fuels.

We use a flow method wherein a weighed amount of fraction is totally vaporized by a measured amount of gas. Figure 1 shows the total-vaporization method.

The packed-bed equilibrium cell contains a known amount (typically 0.3 grams) of heavy narrow-boiling fraction. Gas at high pressure flows slowly through the equilibrium cell. After expansion to ambient pressure, the saturated gas flows to a wet test meter which measures the amount of gas passed through the equilibrium cell.

Shortly downstream from the expansion valve, a small gas sample (about 0.75 cm$^3$) is removed periodically (typically, once every 45 minutes). This gas sample is flushed with helium into a gas-liquid chromatograph for qualitative analysis. This analysis gives a yes or no answer to the question: does the gas sample contain any heavy components? If yes, there is some heavy material in the equilibrium cell. If no, there is no heavy material in the equilibrium cell; it has all vaporized. When qualitative analysis switches from yes to no, the
corresponding gas volume (wet test meter) is the amount of gas needed to vaporize totally the known amount of heavy liquid. The amount of gas and the mass of the material vaporized give the desired solubility. The experimental procedure is completely automated once steady-state gas flow is attained.

We have used the total-vaporization method to measure solubilities of two coal-tar fractions (from a Lurgi coal gasifier) in compressed methane in the region ambient to 70 bar and 150 to 275°C. Table 1 shows the results.

That is the essence of the method. In practice, data reduction is more complicated because, even in a narrow-boiling mixture, there is the stripping effect; the more volatile components vaporize first, the less volatile components vaporize last, and the yes-no transition in the chromatograph is not as sharp as that observed when the heavy material is a pure component. We do not here go into details because these are fully discussed elsewhere (Monge and Prausnitz, 1981; Monge, 1982). Our purpose here is only to call attention to an experimental method that we have operated successfully and that may be useful for a variety of phase-equilibrium problems, especially for synthetic-fuel and food-processing technology.
Literature Cited


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Kurnik, R. T., and Reid, R. C., Fluid Phase Equilibria, 8, 93 (1982)


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### Table 1

**Solubilities of Two Coal-Tar Fractions**

in Methane

<table>
<thead>
<tr>
<th>Fraction</th>
<th>T, °C</th>
<th>P, bar</th>
<th>(10^2) mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>150</td>
<td>3.79</td>
<td>0.336</td>
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<td></td>
<td>170</td>
<td>42.5</td>
<td>0.132</td>
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<tr>
<td></td>
<td></td>
<td>70.0</td>
<td>0.144</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.79</td>
<td>2.21</td>
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<tr>
<td></td>
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<td>42.5</td>
<td>0.313</td>
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<td>0.276</td>
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<td>225</td>
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<td>70.3</td>
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<td>0.133</td>
</tr>
<tr>
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<td>250</td>
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<tr>
<td></td>
<td></td>
<td>42.6</td>
<td>0.365</td>
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<td>70.0</td>
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<td>70.1</td>
<td>0.505</td>
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</table>

---

# Coal tar from Lurgi gasifier (SASOL, South Africa)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Ave. Boiling Point, °C</th>
<th>Average Molec. Wt.</th>
<th>H/C Ratio</th>
<th>Fraction Aromaticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
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<td>187</td>
<td>1.14</td>
<td>0.69</td>
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<tr>
<td>9</td>
<td>359</td>
<td>227</td>
<td>1.18</td>
<td>0.65</td>
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</tbody>
</table>
TOTAL-VAPORIZATION APPARATUS FOR MEASURING THE SOLUBILITY
OF A HEAVY FOSSIL-FUEL FRACTION IN A COMPRESSED GAS
CONTAINING WATER

Figure 1.
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