Solubility of menadione and dichlone in supercritical carbon dioxide

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Abstract

This work reports the solubility of menadione (2-methyl-1,4-naphthoquinone) and dichlone (2,3-dichloro-1,4-naphthoquinone) in SuperCritical (SC) carbon dioxide (CO2) at 313, 323, and 333 K and (7.1–33) MPa. A Gibbs-Duhem test was applied to assess the thermodynamic consistency of experimental data using the Peng-Robinson equation of state with Wong-Sandler mixing rule to represent the solubility, and the non-random two-liquid model to compute Gibbs' excess free energy. In addition, the solubility of menadione and dichlone in SC-CO2 at 313 K and 9.5 MPa, a solubility correction by a change in the density of SC-CO2 as compared to this reference condition (580 kg/m3), and a solubility correction by a change in absolute temperature compared to 313 K were estimated using Chrastil's equation. The solubility of menadione at the reference conditions was 8.3 times higher than that of dichlone (3095 versus 375 mg kg−1 solute/CO2). However, both CO2 density and system absolute temperature had anomalously smaller effects on the solubility of menadione than dichlone, so that menadione was only 4.2 time more soluble in SC-CO2 than dichlone at the extreme conditions of 333 K and 33 MPa (3460 versus 831 mg kg−1 solute/CO2) for which ρ = 851.1 kg/m3. The anomalous behavior of the solubility of menadione in SC-CO2 was imputed to experimental difficulties (solute precipitation resulting in tube blocking, saturation of HPLC detector signal) associated with high solubility values (≥0.5 × 10−3 M fraction) that may have been also responsible for thermodynamically inconsistent results reported by others in literature. We compared the solubilities in SC-CO2 of menadione and dichlone with those for several solutes sharing the same molecule core (1,4-naphthoquinone) and concluded they are negatively impacted by polar and non-polar substituents, but that these negative steric and polarity effects could be partially compensated by a non-polar olefin substituent, or ameliorated by distancing substitutions from the carbonyl groups.

Keywords

Chrastil's equation, Dichlone, Menadione, Solubility, Supercritical CO2, Thermodynamic consistency.