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Solubility Measurement and Correlation of $Cu(tmhd)_2$ and $Mn(pmcp)_2$ in Mixture of $scCO_2$ + H_2 for Supercritical Fluid Deposition

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Solubility of Cu and Mn complexes, bis-(2,2,6,6-tetramethyl-3,5-heptanedionato)copper [$Cu(tmhd)_2$] and bis-(pentamethyl-cyclopentadienyl)manganese [$Mn(pmcp)_2$], in mixture of $scCO_2$ + H_2 was measured. H_2 addition into $scCO_2$ was found to hinder the dissolution of the Cu compound, while it has less impact on the Mn compound. Obtained results were fitted to semi-empirical density-based equations derived from the Mendez-Santiago-Teja equation. It enables prediction of the solubility in the binary solvent, and thus offers a viable tool in the process development of supercritical fluid deposition (SCFD) of Cu and Mn.

SCFD of metals, which is a reduction of metal organics in $scCO_2$ by a reductant, H_2 for instance, is reported to be a promising technology for the fabrication of electronic devices due to its conformal deposition capability on extremely high-aspect-ratio features. Frameworks to correlate and predict the solubility of the precursors under SCFD conditions is essential to design mass production equipments, to ensure feeding at high concentrations without precipitation, and to reveal the process window of SCFD. Although there are many solubility reports for pure $scCO_2$, that for the binary solvent system is missing. We therefore measured the solubility of $Cu(tmhd)_2$ and $Mn(pmcp)_2$ in $scCO_2$ + H_2 systems using in situ UV-vis spectrometry. The solute molar extinction coefficient was evaluated from a calibration curve based on pure $scCO_2$. Reproducibility of the results was confirmed by multiple measurements under our typical condition. The validity of our method was confirmed via comparison of the results in pure $scCO_2$ with literature values. $Cu(tmhd)_2$ showed temperature and pressure dependence in both pure $scCO_2$ and the binary solvent, while $Mn(pmcp)_2$ was nearly independent of both in the two solvent systems under our measured conditions (11-19 MPa, 40-100°C). H_2 addition into $scCO_2$ lowered the $Cu(tmhd)_2$ solubility, whereas the effect was less for the $Mn(pmcp)_2$, where CO_2 density and temperature used in this measurement was kept constant. These results suggest that particular attention should be paid in equipment design and process conditions for Cu deposition, while not so much for Mn. Obtained results were then fitted to four semi-empirical equations for binary solvents derived from the Mendez-Santiago-Teja equation.