RESUMEN

El conocimiento del equilibrio entre fases considerando la precipitación de sólidos para sistemas de gran asimetría en tamaño molecular o en interacciones moleculares, es fundamental para identificar condiciones factibles u óptimas para el procesamiento de estas mezclas complejas.

En la presente tesis se estudia el comportamiento de fases en mezclas binarias asimétricas considerando la presencia de fases sólidas, en amplios rangos de temperatura, presión y composición desde tres perspectivas fundamentales: 1) el estudio y desarrollo de enfoques de modelado que permiten describir el comportamiento de fases; 2) el desarrollo de herramientas para el cálculo del equilibrio entre fases; y 3) el estudio experimental de este tipo de mezclas.

Diferentes enfoques de modelado para describir el comportamiento de las fases sólidas son considerados, y sus ventajas y desventajas son analizadas. En todos los casos se acopla una ecuación de estado, de la familia de van der Waals, para la descripción del comportamiento de las fases fluidas del sistema. En esta tesis, la característica distintiva del modelado de fases sólidas es la reproducción del equilibrio sólido-fluido del compuesto pesado precipitante ("límite del compuesto puro"), a lo cual no se le había dado la debida importancia en la literatura. Algunos de los enfoques propuestos permiten, en principio, una representación satisfactoria del comportamiento de fases sólido-fluido en mezclas asimétricas en un amplio rango de condiciones de temperatura, presión y composición. De este modo, posibilitan en principio la determinación, bastante confiable, de las regiones de miscibilidad completa e inmiscibilidad de las mezclas estudiadas.

Para el cálculo del equilibrio entre fases en las mezclas binarias estudiadas se emplean algoritmos basados en métodos de continuación numérica que permiten computar curvas (o hipercurvas) de equilibrio bifásicas (sólido-fluido) y trifásicas (sólido-fluido-fluido) altamente no lineales, así como también la obtención de puntos de coexistencia de cuatro fases (puntos cuádruples - Q); y de puntos críticos terminales donde se encuentran en equilibrio una fase fluida crítica con una fase sólida. Los resultados obtenidos se presentan en forma de proyecciones (*PT*, *Txy*, *Pxy*) de las líneas

de equilibrio univariantes y de los puntos invariantes del sistema binario (este tipo de diagramas se denomina "diagrama global de fases" en esta tesis). Además, en la presente tesis se extiende al caso sólido-fluido un método sistemático de generación de cortes (isopléticos, isobáricos e isotérmicos) de las superficies de equilibrio entre fases que existen en el espacio presión-temperatura-composición.

Considerando la importancia de determinar la estabilidad de los equilibrios sólido-fluido calculados, en esta tesis se implementó por primera vez un test de estabilidad robusto y computacionalmente económico aplicable al cálculo de isopletas binarias sólido-fluido para identificar sus tramos estables. La estrategia propuesta puede extenderse sistemáticamente a otros equilibrios bifásicos y trifásicos.

Esta tesis aporta además nuevos datos de equilibrio bifásico (fluido-fluido y sólido-fluido) y trifásico (líquido-líquido-vapor y sólido-fluido-fluido) para los sistemas: dióxido de carbono + n-eicosano y propano + n-eicosano. Los datos de equilibrio se obtuvieron por la técnica de First Freezing Point, utilizando una celda de volumen variable (método sintético no analítico). Para el sistema CO_2 + n-eicosano se obtuvieron datos de equilibrio: **[a]** líquido-líquido (LL) en el rango de temperaturas desde 303.15 K hasta 333.45 K (rango de presión: desde 71.6 hasta 169.2 bar, rango de fracción molar de n-eicosano ($x_{n\text{-}C20H42}$) en fase líquida saturada desde 0.001571 hasta 0.004777), **[b]** sólido-líquido (SL) en el rango de temperaturas desde 299.45 hasta 301.55 K (rango de presión de 81.1 a 140.9 bar, rango de $x_{n\text{-}C20H42}$ en fase líquida: de 0.003142 a 0.004777), y **[c]** sólido-líquido-líquido (SLL) en el rango de temperatura de 300.05 K a 302.95 K, y de presión de 71.2 a 250 bar. También se obtuvieron algunos datos de equilibrio líquido-líquido-vapor (LLV) para este sistema en el rango de temperatura entre 300.85 K y 305.25 K, y de presión de 67.4 a 76 bar. En tanto que para el sistema propano + n-eicosano, se midieron: **[a]** isopletas líquido-vapor (LV) en el rango de temperaturas entre 288.55 K y 333.45 K (rango de presión: desde 8.4 a 21.9 bar, rango $x_{n\text{-}C20H42}$ en fase líquida: desde 0.009816 a 0.747668), y **[b]** transiciones sólido-líquido (SL) a composición constante (isopletas SL) en el rango de temperaturas entre 287.05 K y 307.25 K (rango de presión: desde 10.3 a 22.5 bar, rango de $x_{n\text{-}C20H42}$ en fase líquida: desde 0.113130 a 0.747668).

Por último, se presentan los resultados del modelado y cálculo del comportamiento de fases de las mezclas estudiadas experimentalmente y de otros sistemas binarios asimétricos (cuyos datos experimentales se encuentran disponibles en la literatura); los cuales ponen en evidencia la importancia de combinar modelos apropiados, técnicas convenientes de parametrización, y algoritmos robustos de cálculo para la obtención de información del equilibrio entre fases fluidas y sólidas en estos sistemas en amplios rangos de condiciones.

ABSTRACT

The knowledge of the solid-fluid equilibria of systems with large asymmetry in molecular size or in molecular interactions is relevant for the synthesis and optimization of processes dealing with such complex mixtures.

In the present work, we study the phase behavior of asymmetric mixtures, accounting for the presence of solid phases, in wide ranges of temperature, pressure, and composition, from three standpoints: 1) the study and development of modeling approaches for describing the phase behavior of such mixtures; 2) the definition and development of algorithms for the calculation of such phase equilibria; and 3) the experimental study of this type of mixtures.

We consider different modeling approaches for describing the behavior of solid phases. We identify their strengths and limitations. On the other hand, for the description of the fluid phases, we use an equation of state of the van der Waals family. In the present work, the solid-fluid equilibria is described paying close attention to the reproduction of the solid-liquid equilibrium conditions of the precipitating compound ("pure compound limit"), which, in most cases, has not been explicitly considered in the literature. Some of the studied approaches give an acceptable reproduction of the solid-fluid behavior of binary asymmetric mixtures, in wide ranges of temperature, pressure and composition. In this way, a quite reliable computation of regions of complete and partial miscibility is in principle possible for the studied mixtures.

We calculate the phase equilibria for the studied binary mixtures using algorithms based on numerical continuation methods which make it possible to track highly non-linear two-phase (solid-fluid) and three-phase (solid-fluid-fluid) equilibrium curves (or hypercurves). They also facilitate the calculation of points where four phases coexist (quadruple points, Q), and of critical end points, where a critical phase coexists with a solid phase. We present the obtained results in the form of different projections (*PT*, *Txy*, *Pxy*) of univariant equilibrium lines and nonvariant equilibrium points, of the binary system (such diagrams are called "global phase equilibrium diagrams" in this work). Additionally, in this thesis we extend to the solid-fluid case a systematic method for the

generation of isothermal and/or isobaric and/or isoplethic cuts of the phase equilibrium surfaces that develop in the pressure-temperature-composition space.

Considering the importance of evaluating the thermodynamic stability of the calculated solid-fluid equilibria, in this work we implemented, for the first time, a robust and computationally inexpensive stability test. We apply this stability test to the identification of stable segments of binary solid-fluid equilibrium isopleths. The proposed strategy can be systematically extended to other two-phase and three-phase equilibria.

In this work we also report new experimental two-phase (fluid-fluid and solid-fluid) and three-phase (liquid-liquid-vapor and solid-fluid-fluid) equilibrium data for the binary asymmetric systems propane (C_3H_8) + n-eicosane (n-$C_{20}H_{42}$) and carbon dioxide (CO_2) + n-eicosane (n-$C_{20}H_{42}$). We obtained the experimental data through the First Freezing Point technique, using a variable-volume view cell. This corresponds to a synthetic non-analytic method.

For the system carbon dioxide + n-eicosane, we obtained: **[a]** liquid-liquid (LL) equilibrium data (*T* range: 303.15 to 333.45 K, *P* range: 71.6 to 169.2 bar, liquid phase n-eicosane mole fraction (x_{C20}) range: from 0.001571 to 0.004777); **[b]** SL data (*T* range: 299.45 to 301.55 K, *P* range: 81.1 to 140.9 bar, liquid phase x_{C20} range: from 0.003142 to 0.004777); and **[c]** solid-liquid-liquid (SLL) equilibrium experimental data (*T* range: 300.05 to 302.95 K, *P* range: 71.2 to 250 bar). We also obtained some liquid-liquid-vapor (LLV) equilibrium experimental data for system carbon dioxide + n-eicosane (*T* range: 300.85 to 305.25 K, *P* range: 67.4 to 76 bar). For the system propane + n-eicosane, we measured: **[a]** liquid-vapour (LV) isopleths in the temperature (*T*) range from 288.55 K to 333.45 K (Pressure (*P*) range: from 8.4 to 21.9 bar, liquid phase n-eicosane mole fraction (x_{C20}) range: from 0.009816 to 0.747668), and, **[b]** solid-liquid (SL) transitions at constant composition (SL isopleths) in the *T* range from 287.05 K to 307.25 K (*P* range: 10.3 to 22.5 bar, liquid phase x_{C20} range: from 0.113130 to 0.747668).

Finally, we present modeling and calculation results of the phase behavior, both, for the experimentally studied mixtures and for other binary asymmetric systems (whose experimental data are available in the literature). Such results highlight the importance of combining proper models, suitable parameterization techniques and robust calculation algorithms to obtain solid-fluid equilibrium information in wide ranges of conditions.

PT	Relativo a un plano, espacio o diagrama Presión-Temperatura
PVTx	Relación presión-volumen-temperatura-composición
Pxy	Diagrama de equilibrio entre fases en el plano presión-composición, a temperatura constante
RK	Redlich y Kwong
SF	Sólido-fluido
SFF	Sólido-fluido-fluido
SL	Sólido-líquido
SLL	Sólido-líquido-líquido
SLV	Sólido-líquido-vapor
SRK	Soave, Redlich y Kwong
SV	Sólido-vapor
tpd	Distancia con respecto al plano tangente
TPD	Distancia con respecto al plano tangente reducida (*tpd/RT*)
Txy	Diagrama de equilibrio entre fases en el plano temperatura-composición, a presión constante
UCEP	Punto crítico terminal superior (upper critical endpoint)

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