

A New Thermodynamic Method for Solid-Liquid–Vapor Equilibrium in Ternary Antisolvent Crystallization Systems Using Binary Data

By

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Abstract:

Prediction of the solid-liquid-vapor (S-L-V) equilibrium data for the ternary (CO₂-solvent-solid) systems is needed in the design and analysis of Supercritical Antisolvent (SAS) or Gas Antisolvent (GAS) crystallization processes using CO₂ as the antisolvent. A new model is presented in this paper for the prediction of the ternary (S-L-V) equilibrium compositions from the binary interaction constants of (CO₂-solvent) system and the solid solubility in the solvent at a reference pressure. The model first predicts the ternary liquid phase compositions for the isothermal solid-liquid (S-L) equilibrium from the partial molar volume fraction (PMVF) of the solvent in the binary (CO₂-solvent) system. The solid mole fraction in the ternary liquid mixture is considered proportional to the PMVF of the solvent or the contribution of the solvent to the molar volume of the binary (CO₂-solvent) mixture. The bubble point pressure and the vapor phase compositions are calculated ensuring that all three (S-L-V) phases are in equilibrium. The model has been validated for two ternary systems: (CO₂-toluene-naphthalene) and (CO₂-toluene-phenanthrene) with the experimental data from the literature. The predicted bubble point pressures are found to agree well with the corresponding experimental data within % AARD of 3.11 and 1.15 respectively for the two ternary systems at 298 K over the pressure range of 14.9 – 62.4 bar. The variation of pressure with temperature at the S-L-V equilibrium also agrees with the reported trends. The model has been illustrated for the generation of ternary phase diagrams for assessing the crystallization pathways.

Introduction:

It is well known that the supercritical antisolvent (SAS) or gas antisolvent (GAS) crystallization process entails attainment of a very rapid, essentially uniform and very high supersaturation upon reduction of the solid solute solubility in its solution with dissolution of antisolvent CO₂ [1]. This owes to the two-way mass transfer of CO₂ and the solvent, for dissolution of CO₂ and evaporation of solvent respectively. This facilitates uniform nucleation and almost instantaneous crystallization, which make the antisolvent crystallization a unique process resulting in the formation of ultra-fine particles with a narrow particle size distribution and controlled morphology. For calculation of the concentrations at the interface for the two-way mass transfer rates of CO₂ and solvent and for selection of operating conditions for the desired crystallization pathways, it is imperative to have the knowledge of the S-L-V equilibrium compositions for the ternary (CO₂-solvent-solid) system. Three kinds of data are usually generated for ternary systems at the S-L-V equilibrium, namely (i) the liquid phase compositions at a fixed temperature with increasing pressure, i.e., $P-x_1-x_2-x_3$ on a prism, (ii) P-T trace for S-L or L-V equilibrium for a fixed solute to solvent molar ratio in the liquid phase and (iii) the P-T trace for S-L-V equilibrium. The objective of this paper is to generate isothermal and isobaric ternary S-L-V equilibrium compositions and pressure-temperature behavior (P-T trace) of the S-L-V line at constant compositions. Different approaches to modeling the ternary S-L-V equilibrium reported in the literature, essentially differ only in the calculation procedure adopted for the S-L

equilibrium. For example, the isothermal liquid phase compositions at the ternary S-L equilibrium for different pressures were calculated by either (i) the expanded liquid EOS and activity coefficient model or (ii) the EOS model. An accurate yet simpler thermodynamic model is proposed in this work, which involves the solid-liquid (S-L) equilibrium calculations from the partial molar volume fraction (PMVF) of solvent. Subsequently, the iso-fugacity criterion for the L-V equilibrium is considered in order to predict the bubble point pressures so that all three (S-L-V) phases coexist. In this approach, the ternary liquid and vapor phase mole fractions are calculated from the binary (solvent-CO₂) interaction constants and the solid solubility at a reference pressure, for predicting the S-L-V equilibrium of the ternary (CO₂-solvent-solid) system.

Modeling S-L-V Phase Equilibrium:

Pursuing an accurate thermodynamic description of a 3-component system involving a supercritical antisolvent 1, a liquid solvent 2, and the solid solute 3 to be crystallized out, the (S-L-V) phase equilibrium can be modeled after fixing the pressure and temperature, as there are only two degrees of freedom according to the Gibb's phase rule. There are five unknown compositions as the solid is assumed to be crystalline and pure with negligible solubility in the vapor/fluid phase. Two of these unknown mole fractions are eliminated by the constraints that the mole fractions in each phase sum up to unity. In order to find the three unknown mole fractions, namely, x_1 , x_3 and y_2 , the relevant phase equilibrium equations for the three components are:

$$\bar{f}_1^v(T, P, y_1) = \bar{f}_1^L(T, P, x_1) \quad ..(1)$$

$$\bar{f}_2^v(T, P, y_2) = \bar{f}_2^L(T, P, x_2) \quad ..(2)$$

$$f_3^S(T, P) = \bar{f}_3^L(T, P, x_3) \quad ..(3)$$

The vapor-liquid (V-L) equilibria of the antisolvent, 1 and solvent, 2 are described by the respective fugacity coefficients which can be calculated by employing an equation of state. Equations (1) and (2) are expressed in terms of the respective fugacity coefficients as:

$$y_1 \bar{f}_1^v = x_1 \bar{f}_1^L \quad (4)$$

$$y_2 \bar{f}_2^v = x_2 \bar{f}_2^L \quad (5)$$

For the solid-liquid (S-L) equilibrium for the solid solute, 3 equation (3) was expressed by Dixon and Johnston [3] in terms of the activity coefficient and the solid phase properties as:

$$\bar{f}_3^L = \gamma_3 x_3 f_3^{oL} \quad .. \quad (6)$$

$$f_3^S(T, P) = P_3^S \phi_3^S \exp[v_3^S(P - P_3^S) / RT] \quad .. \quad (7)$$

Dixon and Johnston [3] employed the expanded-liquid equation of state model in conjunction with the regular solution theory for the liquid phase activity coefficient of the solid component, γ_3 with a pressure correction and the P-R EOS with all three binary interaction constants for the fugacity coefficients. The solute solubilities of naphthalene and phenanthrene in toluene with CO₂ at 298 K could be reasonably predicted, both at high pressures and low pressures [3]. Kikic et al. [4] suggested an EOS model in which the solid state fugacity of the pure solute, f_3^S was computed from the heat of fusion at the triple point, the triple point temperature T_{tp} , triple point pressure P_{tp} and the fugacity of the pure solute at the fictitious sub-cooled liquid state, f_3^L at the given temperature and pressure [5] as:

$$\ln f_3^S(T, P) = \ln f_3^L(T, P) + (v_3^S - v_3^L)(P - P_{tp}) / RT - \frac{\Delta H_3^f}{RT_{tp}} \left(\frac{T_{tp}}{T} - 1 \right) \quad (8)$$

where, v_3^S and v_3^L are respectively the molar volumes of the solid and liquid phases and f_3^L was calculated by using the P-R EOS. The solute mole fraction, x_3 in liquid phase was obtained iteratively from equation (3) in which \bar{f}_3^L was calculated, in terms of the fugacity coefficients using the PR EOS. This model was tested by Kikic, et al. [4] for naphthalene, phenanthrene and β -carotene in toluene with CO₂ at 298 K with good agreement in correlating the liquid phase compositions. The method suggested by Badilla et al. [6] for modeling the S-L-V equilibrium is similar to that by Kikic et al.[4] excepting that the solid state fugacity of the solute, $f_3^S(T,P)$ was calculated from equation (7) and the sublimation pressure, P_3^S was predicted from the triple point pressure and temperature, and the heat of sublimation.

In case, the solute mole fraction in the vapor phase, y_3 can not be neglected, the S-L-V equilibrium can also include the solid-vapor equilibrium for the solid solute as:

$$f_3^S(T,P) = \bar{f}_3^V(T,P, y_3) \quad ..(9)$$

Accordingly,
$$y_3 = \frac{P_3^S f_3^S \exp[v_3^S P / RT]}{P \bar{f}_3^V} \quad .. (10)$$

Shariati and Peters [7] correlated the S-L-V equilibrium data for salicylic acid (2-hydroxy benzoic acid)–1-propanol–CO₂ using the Stryjek-Vera modification of Peng-Robinson (P-R-S-V) EOS in conjunction with equation (8) for the solid state fugacity of solute [7], as described earlier. This procedure also yielded good agreement of the liquid phase compositions of salicylic acid in the temperature and pressure ranges of 273-367 K and 1.0 -12.5 MPa. The P-T traces of S-L and L-V equilibria were calculated for a fixed solute concentration on CO₂-free basis and subsequently the P-T trace for the S-L-V equilibrium from the point of intersection of these two lines. However, all these methods are very tedious and complicated as these require lots of solid properties and two binary interaction constants for each pair which are not readily available and the estimation of which often leads to uncertainties.

Proposed Model for Ternary S-L-V Equilibrium:

It was reported earlier that the relative partial molar volume reduction (RPMVR) of the solvent in a binary (solvent- CO₂) mixture is the criterion for the solute solubility reduction in the ternary (solute- solvent- CO₂) system with CO₂ dissolution [1]. The high supersaturation achieved in the antisolvent crystallization process is characterized by a sharp reduction in the partial molar volume of the solvent, \bar{v}_2 at a high CO₂ dissolution, X_1 . The sharp reduction of \bar{v}_2 , even to its negative values, substantiates the fact that CO₂ molecules cluster around the solvent molecule causing it to lose its affinity for the solute molecules. . As a result the secluded solute molecules aggregate causing nucleation followed by crystallization. The solvent power of the CO₂-diluted solvent may thus be interpreted as the capacity of the partially clustered solvent molecules by the antisolvent CO₂ molecules to retain their affinity for the solute molecules [2]. Accordingly the solute mole fraction, x_3 in the ternary system for the S-L equilibrium, can be calculated with good accuracy from PMVF of the solvent, defined as $(1-X_1)\bar{v}_2/v$, in the binary (solvent-CO₂) liquid mixture using the equation:

$$x_3(T,P) = \frac{(1-X_1)\bar{v}_2(T,P,X_1)/v(P,X_1)}{(1-X_{10})\bar{v}_2(T,P_0,X_{10})/v(P_0,X_{10})} \cdot x_{30}(T,P_0) \quad ..(11)$$

where $x_3 = X_3(1-x_1)$ and $x_1 = X_1(1-x_3)$ whereas x_{30} is the solute mole fraction in the ternary system at the reference pressure, P_0 . PMVF is thus a characteristic parameter of the binary (CO₂-solvent) system in which the mole fraction of CO₂ is X_1 . PMVF varies between 1 and 0 as X_1 varies from 0 to 1. The negative values of \bar{v}_2 indicate a very high supersaturation at which x_3 is nearly zero.

The P-R EOS with the binary interaction constants [8] is employed for the calculation of v and \bar{v}_2 at different values of X_1 using equations (12) and (13):

$$\bar{v}_2 = [v - X_1 \left(\frac{\partial v}{\partial X_1} \right)_{P,T}] \quad (12)$$

$$v = X_1 \bar{v}_1 + X_2 \bar{v}_2 \quad (13)$$

$$\text{where, } \bar{v}_i = \left(\frac{\partial V}{\partial n_i} \right)_{P,T} \quad (14)$$

The proposed model involves first generation of isothermal ternary (x_1 - x_2 - x_3) liquid phase compositions for the S-L equilibrium from the molar volume, v of the binary (CO₂-solvent) liquid solution at different CO₂ mole fractions or pressures and the solid solubility x_{30} . Both solute-solvent and solvent-antisolvent interactions are considered in the terms, x_{30} and PMVF of the solvent respectively for the solid-liquid (S-L) equilibrium (having three degrees of freedom). Then, for the co-existence of three (S-L-V) phases, the vapor-liquid (V-L) equilibrium is considered for finding the bubble point pressures and the vapor phase compositions based on the iso-fugacity criterion for the components 1 and 2 as given by equations (1) and (2). This is repeated for other temperatures to obtain the P-T trace of the S-L-V equilibrium at constant ternary compositions.

Results and Discussion:

This approach has been utilized for the S-L-V Equilibrium of a large number of ternary systems. In this paper only the mole fractions of naphthalene and phenanthrene in toluene-CO₂ mixtures have been presented. **Figures 1 and 2** show the effect of temperature on the S-L-V predictions and an excellent agreement of the calculated and experimental S-L-V pressure-composition data at 298 K for the two systems respectively. The present model has yielded very good agreement within 3.11 and 1.15 % AARD in the bubble point pressures for the two systems respectively at 298 K over the pressure range of 14.9-62.4 bar. This method is much simpler and more reliable than the rigorous methods reported earlier requiring calculation of x_3 from the fugacity of the solute in the solid and liquid states in a complicated way using an equation of state. It is also observed that the presence of the nonvolatile solute like phenanthrene has negligible effect on the vapor phase mole fractions of toluene and CO₂, as these for the ternary system are very much close to those for the binary (toluene and CO₂) system at the same pressure and 298 K. The P-T trace for the constant liquid phase compositions at the S-L-V- equilibrium is obtained from the isothermal plots of P vs. ($x_3/1-x_3$) at three temperatures and is shown in **Figure 3**. It can be seen that the pressure required to attain the S-L-V equilibrium increases with temperature at the same composition, and increases with x_3 at constant temperature. This trend is similar to that reported by Kikic et al.[4]. **Figures 4 and 5** depict the effects of variations in pressure and temperature on isothermal and isobaric triangular phase diagrams respectively for naphthalene-toluene-CO₂ system, which have been generated using this new model. It can be seen that with increasing pressure, the isothermal S-L-V region shrinks and gets completely eliminated above the

mixture critical pressure. This indicates that the solid crystallization pathway directly traverses from the S-L to S-V regions above the mixture critical pressure, which is desirable for the solvent-free particles. With increasing temperature, however, S-L-V region expands at a constant pressure.

Conclusions:

The new approach to thermodynamic modeling of the ternary S-L-V equilibrium utilizes the partial molar volume fraction (PMVF) of the solvent in the binary (CO₂-Solvent) liquid mixture and the solid solute solubility at a reference pressure. The PMVF of solvent gives a measure of the solvent power of the solvent diluted with CO₂ in the SAS or GAS process. This model entails first prediction of the isothermal ternary liquid mole fractions for the S-L equilibrium using binary (solvent-antisolvent) interaction constants at different CO₂ mole fractions or pressures prior to the usual V-L-E calculations. This method has yielded good agreement for several systems, as illustrated in this paper for naphthalene-toluene-CO₂ and phenanthrene - toluene-CO₂ systems. The model has been illustrated for generation of the P-T trace at the S-L-V equilibrium and the ternary phase diagrams in order to assess the S-L-V region for selecting the process conditions

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Nomenclature:

- v: molar volume of solution
 \bar{v}_1 : Partial molar volume of CO₂ in a binary mixture of CO₂ and solvent
 \bar{v}_2 : Partial molar volume of the solvent in a binary mixture of CO₂ and solvent
X₁: Mole fraction of CO₂ in liquid phase on solute-free basis
X₂: Mole fraction of the solvent in liquid phase on solute-free basis
x₃: Mole fraction of solid solute in ternary liquid phase
x₁: Mole fraction of CO₂ in ternary liquid phase
y₃: Mole fraction of solid solute in ternary fluid phase

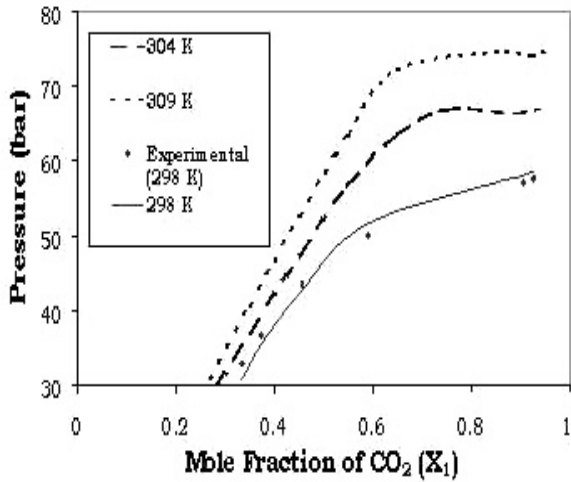


Fig 1: SLVE Pressures for CO₂-toluene-naphthalene

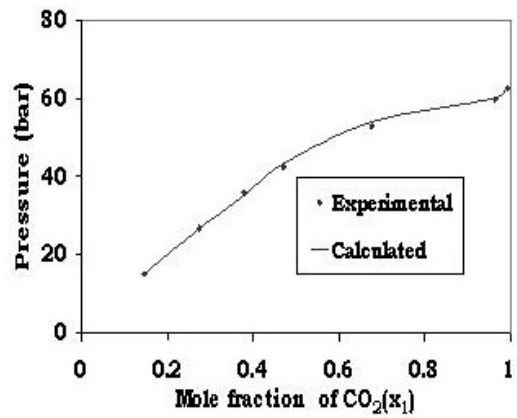


Fig 2: SLVE Pressures for CO₂-toluene-phenanthrene

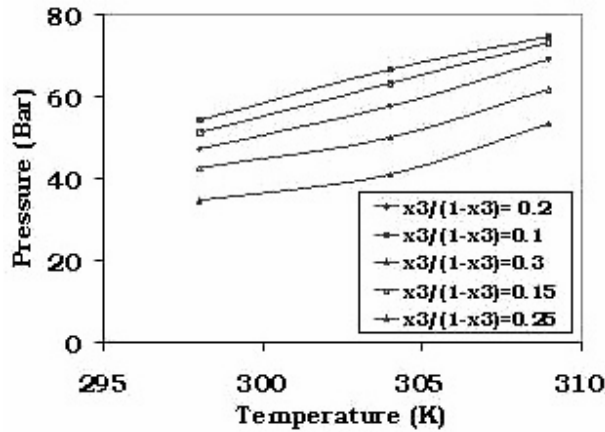


Fig 3: SLVE P-T trace for CO₂-toluene-naphthalene

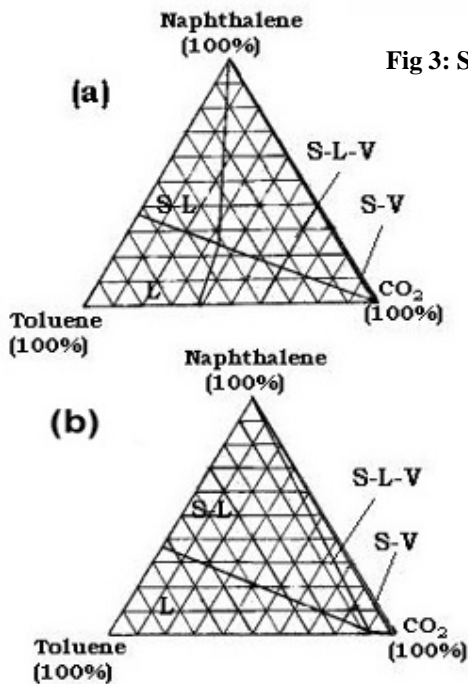


Fig. 4 Effect of pressure on 298 K-ternary phase diagram for CO₂-toluene-naphthalene at (a) 32.9 bar (b) 57.7 bar

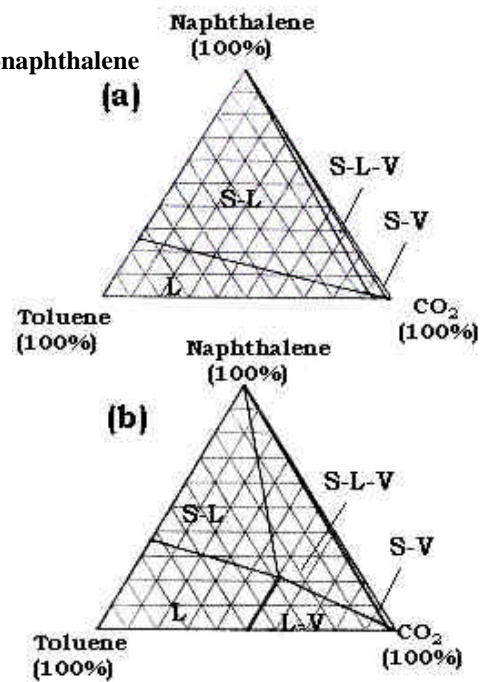


Fig.5 Effect of temperature on 58.2 bar-ternary phase diagram for CO₂-toluene-naphthalene at (a) 298 K (b) 309 K