J. Chem. Eng. Data **2005,** *50,* 1283−1289

New Prediction Method for Ternary Solid−Liquid−Vapor Equilibrium from Binary Data

Mamata Mukhopadhyay* and Sameer V. Dalvi

Chemical Engineering Department, Indian Institute of Technology Bombay, Mumbai 400076, India

A new method is presented in this paper for predicting ternary solid−liquid−vapor equilibrium (S-L-V-E) compositions from the binary interaction constants of the (CO_2 + solvent) system in the Peng−Robinson (P-R) equation of state (EOS) and the solid solubility in the solvent at a reference pressure. This method first employs calculation of the mole fraction of the solid solute in the ternary liquid mixture as proportional to the partial molar volume fraction (PMVF) of the solvent, that is, the contribution of the solvent to the molar volume of the binary (CO_2 + solvent) mixture. Subsequently, vapor−liquid equilibrium (V-L-E) computations are employed for the other two components. The method has been verified in this paper for two ternary systems: (i) CO_2 + toluene + naphthalene and (ii) CO_2 + toluene + phenanthrene. The predicted bubble point pressures at S-L-V-E are found to agree well with the corresponding experimental data from the literature within AARD of ±3.11 % and ±1.15 %, respectively, for the two ternary systems at 298 K over the pressure range of (14.9 to 62.4) bar. The *P*−*T* trace at S-L-V-E also agrees well with the reported trends. The effects of pressure and temperature on ternary-phase diagrams generated by this method are utilized for the assessment of crystallization pathways.

Introduction

It is well-known that the supercritical antisolvent (SAS) crystallization process facilitates attainment of very rapid, essentially uniform and very high supersaturation owing to a rapid reduction[1] of solid solute solubility in the atomized droplets of its solution. This owes to the two-way mass transfer of antisolvent CO_2 and solvent vapor, to and from the solution droplets, respectively. This leads to uniform nucleation and almost instantaneous crystallization, which make SAS a unique process for producing ultrafine particles with a narrow particle size distribution and controlled morphology. For calculation of the mass transfer rates of CO_2 and solvent vapor and for selection of operating conditions for the desired crystallization pathway, it is imperative to have the knowledge of the solid−liquid−vapor equilibrium (S-L-V-E) compositions for the ternary (CO_2 + solvent + solid) system.

Various approaches to modeling ternary S-L-V-E, as reported in the literature, essentially differ only in the procedure adopted for calculation of the solid solute mole fraction in the liquid phase, which is based on the solid−liquid equilibrium (S-L-E) for the ternary system. For example, the isothermal S-L-E was computed at different pressures by using either (i) the expanded liquid EOS along with an activity coefficient model or (ii) the EOS model. Subsequently isothermal V-L-E was considered for CO_2 and solvent for predicting the bubble point pressures at S-L-V-E based on the iso-fugacity criterion. The objective of this paper is to develop a simple, accurate, and reliable prediction method that does not require the solid−liquid thermophysical properties of the solid solute for generation of (i) the isothermal bubble point pressure composition (*P*−*x*−*y*) data of the ternary system at S-L-V-E, (ii) the pressure−temperature behavior (*P*−*T* trace) of the S-L-V-E line at constant compositions, and (iii) the effects of pressure and temperature on isothermal and isobaric triangular-phase diagrams, respectively. The proposed method simply utilizes the partial molar volume fraction (PMVF) of solvent[2,3] in the binary (CO_2 + solvent) system and the solid solubility in the solvent at the ambient pressure for isothermal ternary S-L-E.

Conventional Modeling of Ternary S-L-V-E

Accurate thermodynamic modeling of S-L-V-E of a ternary system comprising the supercritical antisolvent CO_2 (1), the liquid solvent (2), and the solid solute (3) a priori requires the fixing of two variables, such as pressure and temperature, as there are only two degrees of freedom according to the Gibbs phase rule. Out of the five unknown mole fractions (as the solid is assumed to be crystalline and pure with negligible solubility in the vapor or fluid phase), two of them are eliminated by the constraints that the mole fractions in each phase sum up to unity. For finding the remaining three unknown mole fractions, namely, x_1, y_2, and x_3, the relevant equations of the iso-fugacity criterion for the three components at S-L-V-E are given by

$$\bar{f}_1^{V}(T, P, y_1) = \bar{f}_1^{L}(T, P, x_1) \tag{1}$$

$$\bar{f}_2^{V}(T, P, y_2) = \bar{f}_2^{L}(T, P, x_2) \tag{2}$$

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

where, $\bar{f}_i$ is the partial fugacity of component in solution (bar) and f_i is the pure component fugacity (bar). The superscripts V, L, and S represent the vapor, liquid, and solid phases, respectively. It may be noted that the precipitation of solid takes place only if $\bar{f}_3^{L}$ exceeds f_3^{S}, till it equals f_3^{S}.

Equations 1 and 2 represent the iso-fugacity criterion for V-L-E for the components (1) and (2), and the fugacities

---

* Corresponding author. E-mail: mm@che.iitb.ac.in. Telephone: +912225767248. Fax: +912225726895.

10.1021/je050028w CCC: $30.25

are expressed in terms of the respective fugacity coefficients $\bar{\phi}_i^{\mathrm{V}}$ and $\bar{\phi}_i^{\mathrm{L}}$ by

$$y_1\bar{\phi}_1^{\mathrm{V}} = x_1\bar{\phi}_1^{\mathrm{L}} \tag{4}$$

$$y_2\bar{\phi}_2^{\mathrm{V}} = x_2\bar{\phi}_2^{\mathrm{L}} \tag{5}$$

where an appropriate equation of state (EOS), such as the Peng−Robinson (P-R) equation, is employed for calculating the fugacity coefficients.

For S-L-E (eq 3), Dixon and Johnston[4] expressed the solid-phase fugacity in terms of the solid-phase properties with

$$f_3^{\mathrm{S}}(T, P) = P_3^{\mathrm{S}}\phi_3^{\mathrm{S}} \exp[v_3^{\mathrm{S}}(P - P_3^{\mathrm{S}})/RT] \tag{6}$$

where, P_3^{S} is the sublimation pressure, ϕ_3^{S} is the fugacity coefficient at P_3^{S}, and v_3^{S} is the molar volume of the solid solute. The liquid-phase fugacity $\bar{f}_3^{\mathrm{L}}$ of the solid solute in the ternary solution in terms of the liquid-phase activity coefficient γ_3 is given by

$$\bar{f}_3^{\mathrm{L}} = \gamma_3 x_3 f_3^{\mathrm{oL}} \tag{7}$$

The expanded-liquid EOS model[4] was employed in conjunction with the regular solution theory for γ_3 with a pressure correction. The method requires a number of equations and properties of the solid solute, such as the hypothetical liquid-phase fugacity f_3^{oL} at the standard state, fugacity coefficient ϕ_3^{S}, sublimation pressure P_3^{S}, molar volume v_3^{S} at the system temperature, etc., which are not readily available for many solid substances. Their estimation often leads to uncertainties, though the solubilities of naphthalene and phenanthrene in toluene with dissolved $\mathrm{CO_2}$ at 298 K could be reasonably predicted, both at high and low pressures.[4]

Kikic et al.[5] 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 ΔH_3^{f}, the triple point temperature T_{tp}, the triple point pressure P_{tp}, and the fugacity of the pure solute f_3^{L} at the fictitious subcooled liquid state at the given temperature.[6] The model is given by

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

where v_3^{S} and v_3^{L} are the molar volumes of the solid and liquid phases, respectively, and f_3^{L} was calculated by using the P-R EOS. The solute mole fraction x_3 in liquid phase was obtained by iterations using eq 3 in which $\bar{f}_3^{\mathrm{L}}$ was calculated in terms of the fugacity coefficients by using the P-R EOS. The method was validated by Kikic et al.[5] for ternary systems such as naphthalene, phenanthrene, and β-carotene in (toluene + $\mathrm{CO_2}$) liquid mixture at 298 K by getting good agreement with the experimental data. This method also has the limitations that it requires knowledge of solid properties, such as the hypothetical liquid-phase fugacity and the fugacity coefficient of the solid solute. The modeling of S-L-V-E by the method suggested by Badilla et al.[7] is similar to that by Kikic et al.[5] except that the solid-state fugacity of the solute, $f_3^{\mathrm{S}}(T, P)$, was calculated from eq 6 and the sublimation pressure, P_3^{S}, was predicted from the triple point pressure and temperature and the heat of sublimation.

Shariati and Peters[8] correlated the S-L-V-E data for the salicylic acid (2-hydroxy benzoic acid) + 1-propanol + $\mathrm{CO_2}$ system using the Stryjek−Vera modification of the Peng−Robinson (P-R-S-V) EOS in conjunction with eq 8 for the solid-state fugacity of the solute.[6] This procedure yielded good agreement of the liquid-phase compositions of salicylic acid in the temperature range of (273 to 367) K and pressure range of (1.0 to12.5) MPa. The $P-T$ traces for S-L-E and V-L-E were calculated for a fixed solute concentration on a $\mathrm{CO_2}$-free basis and, subsequently, the $P-T$ trace for the S-L-V-E from the point of intersection of these two lines. This method also requires properties of solid solute for computation of the hypothetical liquid-phase fugacity, molar volumes at the solid and liquid states, enthalpy of fusion, triple point temperature and pressure, and fugacity coefficients of the solid solute in the liquid mixture.

In case the solute mole fraction in the vapor phase, y_3, is not insignificant, the S-L-V-E calculations need to include S-V-E as well. Accordingly

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

and

$$y_3 = \frac{P_3^{\mathrm{S}}\,\phi_3^{\mathrm{S}}\exp[v_3^{\mathrm{S}}P/RT]}{P\bar{\phi}_3^{\mathrm{V}}} \tag{10}$$

It is thus clear that there is a long-standing need to develop a simple and a reliable method that obviates the difficulties and limitations in the above-mentioned prediction methods for ternary S-L-V-E.

It is well-known that the instantaneous reduction of equilibrium solubility of the solid solute in the liquid phase by $\mathrm{CO_2}$ dissolution is attributed to the sharp reduction in the partial molar volume (PMV) of the solvent, $\bar{v}_2$, at high $\mathrm{CO_2}$ mole fractions, X_1, where X_1 is the mole fraction of $\mathrm{CO_2}$ in the binary ($\mathrm{CO_2}$ + solvent) mixture.[1,2] A first attempt for the solid solubility prediction at S-L-E in the ternary ($\mathrm{CO_2}$ + solvent + solid) system in terms of $\bar{v}_2$ was made by Chang and Randolph,[9] who had expressed the solid solubility (in mg/mL of solution) as linearly proportional to PMV of solvent. This method was found inaccurate by Kikic et al.[10] for β-carotene, naphthalene, and phenanthrene in toluene diluted with $\mathrm{CO_2}$. However, the original equation of Chang and Randolph[9] was later modified[1] by expressing the solid solubility in terms of its mole fraction and incorporating the pressure dependence of the volume of solution, and then the solid solubility (in mole fraction) on $\mathrm{CO_2}$-free basis could be predicted reasonably well from PMV of the solvent in the binary ($\mathrm{CO_2}$ + solvent) mixture.[1] This method was found adequate for certain solids such as β-carotene, but it was not predictive for solubilities of naphthalene and phenanthrene as these solids have high solubilities in toluene. Subsequently, a new model[2,3] was proposed for ternary S-L-E in terms of PMVF, a characteristic parameter of the $\mathrm{CO_2}$-diluted binary solvent mixture, and this could satisfactorily predict solubilities of a large number of solids in organic solvents with dissolved $\mathrm{CO_2}$.

Proposed Method for Ternary S-L-V-E

Partial Molar Volume Fraction (PMVF) of Solvent. It was reported earlier that the $\mathrm{CO_2}$ dissolution in an organic solvent causes reduction of *PMV* of the solvent, $\bar{v}_2$. Accordingly the relative partial molar volume reduction (RPMVR) of the solvent in a binary ($\mathrm{CO_2}$ + solvent) mixture was proposed as the criterion for antisovent crystallization,

Table 1. Binary Interaction Parameters[4]

pair	k_{ij}
CO_2 + toluene	0.10
CO_2 + naphthalene	0.11
CO_2 + phenanthrene	0.12
toluene + naphthalene	0.0
toluene + phenanthrene	0.0

as it is an indicator of the solute solubility reduction.[1] The sharp reduction of $\bar{v}_2$, even to a negative value, substantiates the fact that the solvent molecules get surrounded by clusters of CO_2 molecules in the liquid phase at high mole fractions of CO_2. This solution-phase clustering is justified by the argument that addition of the solvent molecules (although the pure solvent has a higher molar volume than pure CO_2) leads to a decrease in the total volume of the solution (i.e., negative $\bar{v}_2$) in the presence a very large number of CO_2 molecules which, in turn, cause them to lose their affinity for the solid solute molecules. As a result, the secluded solute molecules aggregate causing nucleation followed by crystallization. The solvent power of the CO_2-diluted solvent is thus attributed to the affinity of the solvent molecules that are partially surrounded by the clusters of CO_2 molecules.[1,2]

Accordingly, PMVF of the solvent, defined as $[(1 - X_1)\bar{v}_2/v]$, depicting the solvent's contribution to the molar volume of the binary solution, characterizes the solvent capacity of the binary (CO_2 + solvent) solution in which the mole fraction of CO_2 is X_1. PMVF varies between 1 and 0, as X_1 varies from 0 to 1. It was demonstrated earlier[3] that eq 11 could be used for calculating x_3, the mole fraction of the solid solute in the ternary liquid mixture at isothermal S-L-E of a large number of solid solutes with good accuracy. This method requires only the knowledge of PMVF of the solvent in the binary (CO_2 + solvent) liquid mixture and the solid solubility x_{30} at a reference pressure, P_0, as:

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

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 liquid mixture at the reference pressure P_0, X_{10} is the mole fraction of CO_2 in the binary (CO_2 + solvent) liquid mixture at P_0, and x_1 is the mole fraction of CO_2 in the ternary (CO_2 + solvent + solid) liquid mixture The negative values of $\bar{v}_2$ imply that x_3 is nearly zero. Both solute−solvent and solvent−antisolvent interactions are considered in x_{30} and PMVF of the solvent, respectively.

Methodology of S-L-V-E Calculations. The binary interaction constants in the van der Waals quadratic mixing rule for the P-R EOS[11] as listed in Table 1 are utilized for calculation of molar volume (MV), v, and partial molar volume (PMV), $\bar{v}_2$, at different values of X_1 using eqs 12 and 13:

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

$$v = X_1\bar{v}_1 + X_2\bar{v}_2 \tag{13}$$

where

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_{j\neq i}} \tag{14}$$

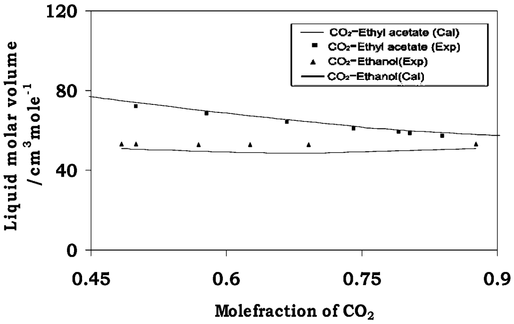

Figure 1. Comparison of liquid molar volumes predicted by the P-R EOS at 298 K with the corresponding experimental data.[12]

The values of PMVF of the solvent are calculated as a function of X_1 at different pressures at a constant temperature; the solute mole fraction, x_3, in the liquid phase is calculated using eq 11 for isothermal S-L-E. Subsequently, eqs 4 and 5 are employed for isothermal V-L-E for the individual components CO_2 and solvent (as the solute mole fraction in vapor phase is assumed negligible) for predicting the bubble point pressures and the vapor-phase compositions for the ternary S-L-V-E. This is repeated for other temperatures to obtain the $P-T$ trace of the S-L-V-E line at constant ternary compositions.

Results and Discussion

The present prediction method for ternary S-L-V-E has been illustrated in this paper only for two systems, namely, (i) CO_2 + toluene + naphthalene and (ii) CO_2 + toluene + phenanthrene, in the absence of the corresponding experimental data available for other systems in the literature. The method of calculation of the liquid molar volume, v, of binary (CO_2 + toluene) mixtures using the P-R EOS with the van der Waals mixing rule was validated in our earlier paper;[1] its agreement with the corresponding experimental data from the literature[12] is demonstrated in Figure 1. The calculation of liquid mole fraction, x_3, of naphthalene and phenanthrene for isothermal S-L-E by eq 11 using PMVF of toluene in the binary (CO_2 + toluene) system was earlier validated,[2] and the agreement with the experimental data from the literature[4] is illustrated in Figure 2, panels a and b, respectively. Relatively larger deviations in the phenanthrene mole fractions in Figure 2b at high CO_2 mole fractions (above 0.7) may be attributed to experimental uncertainties in the measurement of low values of phenanthrene mole fractions. The predictability of eq 11 using PMVF of the solvent calculated by the P-R EOS was earlier satisfactorily validated[3] for a large number of solids in different organic solvents with dissolved CO_2.

The effects of temperature and pressure on MV of the binary (CO_2 + toluene) mixture and PMV and PMVF of toluene in it have been ascertained. It can be seen from Figure 3a,b that MV increases and PMV of toluene decreases with temperature at a constant pressure at high CO_2 mole fractions. Conversely, it can be noted from Figure 4a,b that MV decreases and that PMV of toluene increases with pressure at high CO_2 mole fractions at a constant temperature. However, PMVF of toluene increases with pressure and decreases with temperature as does PMV of toluene, as can be seen from Figure 5a,b. This indicates that both PMVF and PMV of toluene have similar trends and that both are significantly affected at high CO_2 mole fractions, as compared to MV, as MV is a mole fraction-averaged property of the binary mixture. It may be noted that the effects of temperature and pressure on MV and PMV are negligible at low CO_2 mole fractions (less than

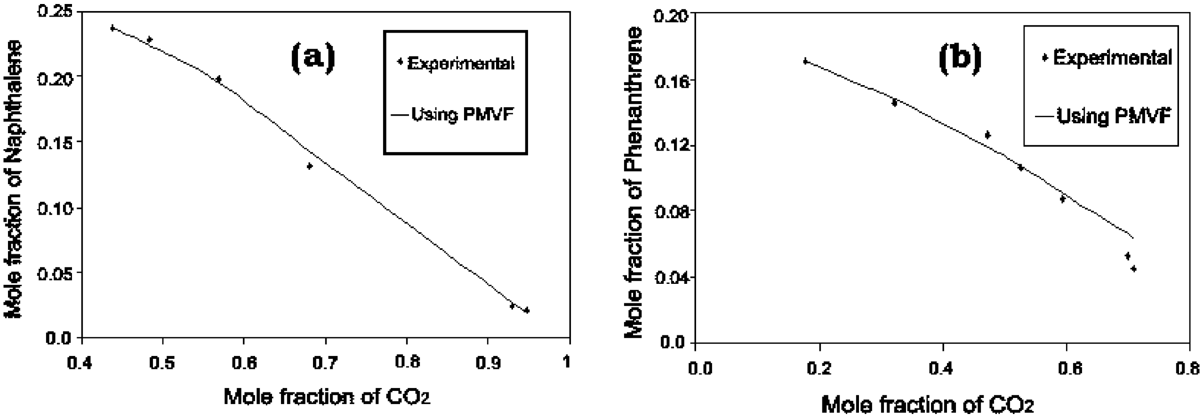

Figure 2. Comparison of predicted solubility of (a) naphthalene and (b) phenanthrene in toluene + CO_2 at 298 K with experimental data.[4]

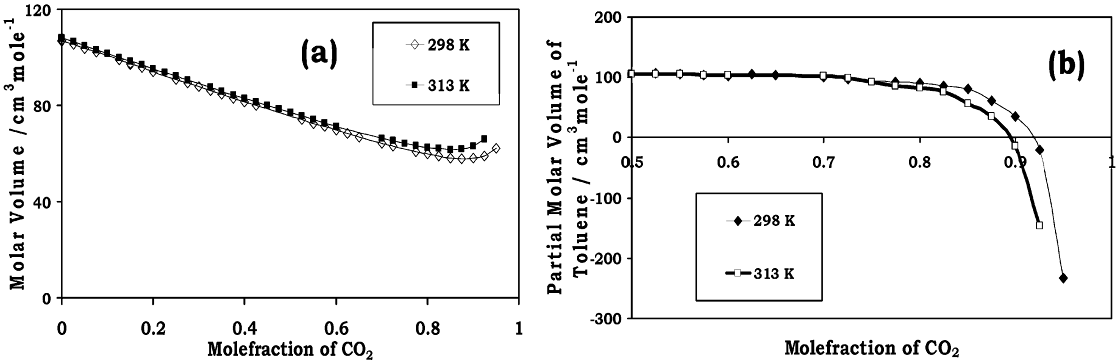

Figure 3. Effect of temperature on (a) MV and (b) PMV in CO_2 + toluene system at 60 bar.

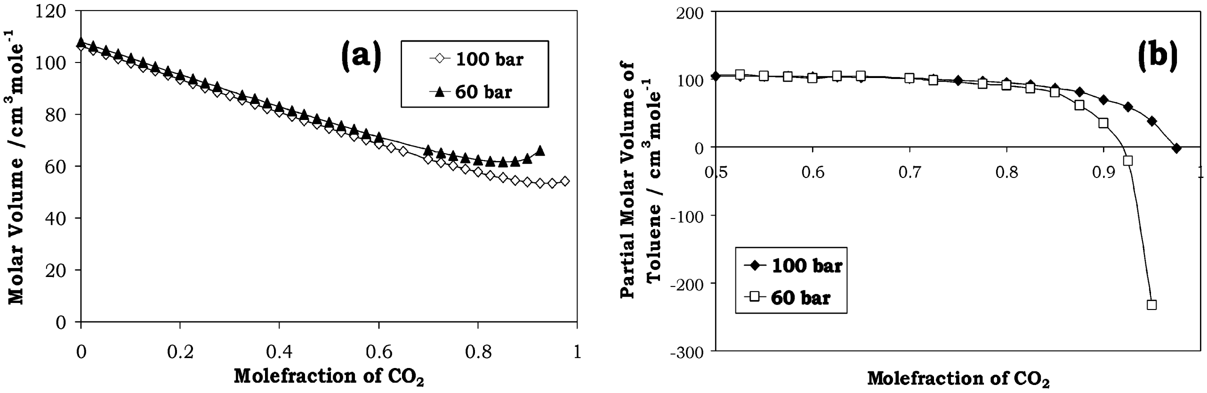

Figure 4. Effect of pressure on (a) MV and (b) PMV in CO_2 + toluene system at 298 K.

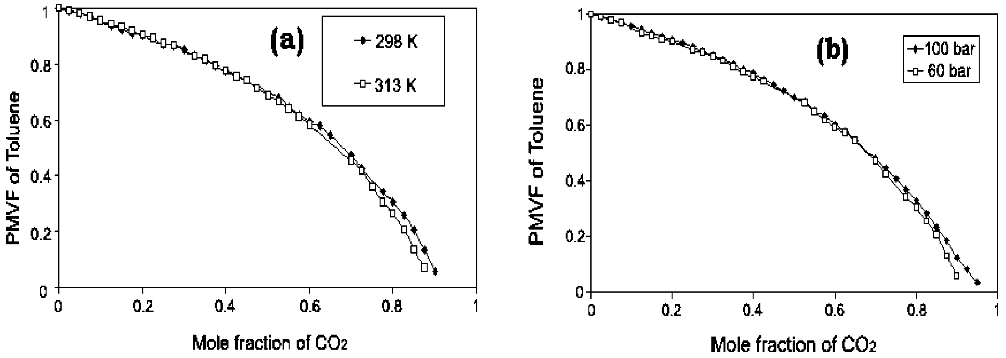

Figure 5. Effect of (a) temperature at 60 bar and (b) pressure at 298 K on PMVF of toluene in CO_2 + toluene system.

0.7), as the solvent is much less compressible than CO_2 and the solution-phase clustering takes place only at high CO_2 mole fractions.

Figure 6a,b shows the effect of temperature on the S-L-V-E predictions. An excellent agreement is observed between the calculated and the experimental S-L-V-E pres-

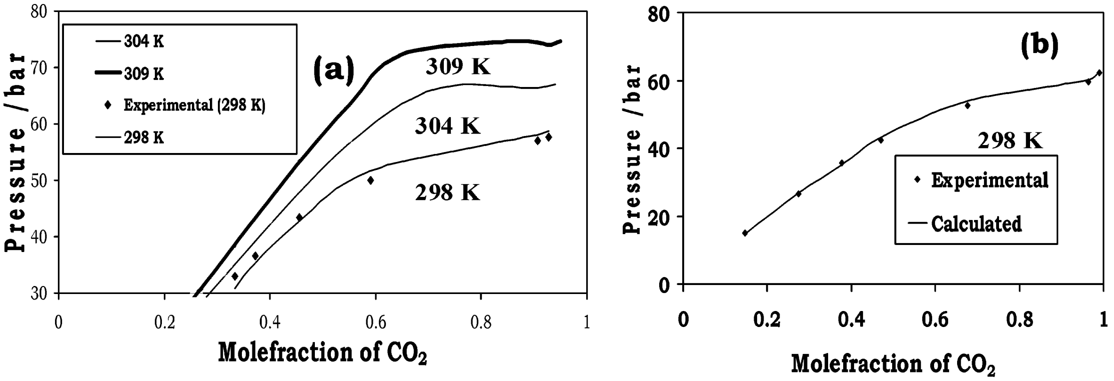

Figure 6. Comparison of predicted S-L-V-E bubble point pressures for ternary systems: (a) naphthalene + toluene + CO_2 and (b) phenanthrene + toluene + CO_2.

Table 2. Comparison of Predicted Bubble Point Pressures with Experimental Data[4] at S-L-V-E System at 298 K

pressure/bar		liquid mole fractions			vapor mole fractions [cal]			ARD[b] in P_{cal}/%
exp[4]	cal[a]	x_1[4]	x_2	x_3 [cal]	y_1	y_2	y_3	
				CO_2 + Toluene + Naphthalene System				
32.9	30.8	0.334	0.4290	0.2370	0.99826	0.01730	0.000018	6.30
36.7	35.3	0.373	0.3980	0.2290	0.99830	0.00163	0.000019	3.62
43.4	42.7	0.456	0.3460	0.1980	0.99827	0.00171	0.000024	1.66
49.9	51.6	0.591	0.2770	0.1320	0.99800	0.00196	0.000033	3.40
57.1	58.2	0.907	0.0688	0.0242	0.99793	0.00200	0.000068	1.84
57.7	58.8	0.928	0.0511	0.0209	0.99809	0.00183	0.000082	1.84
				CO_2 + Toluene + Phenanthrene System				
14.9	14.9	0.147	0.682	0.1710	0.9968	0.0031	0.00001	0.006
26.6	26.8	0.275	0.579	0.1460	0.9977	0.0023	0.00001	0.688
35.7	35.1	0.378	0.426	0.1260	0.9979	0.0021	0.00000	1.597
42.3	43.2	0.470	0.424	0.1060	0.9979	0.0021	0.00000	2.129
52.7	53.9	0.676	0.279	0.0453	0.9976	0.0025	0.00000	2.310
59.6	60.0	0.964	0.035	0.0015	0.9982	0.0018	0.00000	0.754
62.4	62.8	0.991	0.008	0.0005	0.9992	0.0008	0.00000	0.569

[a] AARD: average absolute relative deviation, $1/n\ \mathrm{d}p\Sigma|P_{exp} - P_{cal}/P_{exp}| \times 100 = 3.11$ %. [b] ARD: absolute relative deviation, $|(P_{exp} - P_{cal})/P_{exp}| \times 100$.

Table 3. Comparison of Calculated Vapor-Phase Mole Fractions of CO_2 and Solvent for Ternary (CO_2 + Toluene + Solute) S-L-V-E with Those for Binary (CO_2 + Toluene) V-L-E at 298 K

		calculated vapor-phase mole fractions					
				ternary S-L-V-E			
		binary V-L-E		with naphthalene		with phenanthrene	
pressure/bar[4]	liquid-phase CO_2 mole fractions[4]	CO_2	toluene	CO_2	toluene	CO_2	toluene
32.9	0.334	0.9974	0.00269	0.99826	0.00173	0.9978	0.0022
36.7	0.373	0.9974	0.00269	0.99830	0.00168	0.9979	0.0021
43.4	0.456	0.9974	0.00269	0.99827	0.00171	0.9978	0.0022
49.9	0.591	0.9973	0.00270	0.99800	0.00196	0.9976	0.0024
52.7	0.907	0.9977	0.00231	0.99800	0.00200	0.9979	0.0021
59.6	0.928	0.9977	0.00232	0.99809	0.00183	0.9980	0.0020

sure composition ($P-x$) data at 298 K for both systems. The present model has yielded very good agreement of the bubble point pressures (AARD within ±3.11 % and ±1.15 %) for the two systems at 298 K over the pressure range of (14.9 to 62.4) bar, as can be seen from Table 2. Yet it is simpler than the rigorous methods reported earlier.[4,5,7,8] The vapor-phase compositions for the ternary S-L-V-E have been calculated for both systems from the isothermal ($P-x$) data[4] and have been compared in Table 3 with those for the corresponding binary V-L-E to analyze the effect of the presence of the solid solute in the liquid phase. The calculated vapor-phase compositions for ternary S-L-V-E cannot be compared with the corresponding experimental data, as these data are not reported in the literature for these two systems.

Table 3 also illustrates that the presence of the nonvolatile solute like phenanthrene has a negligible effect on the vapor-phase mole fractions of toluene and CO_2, as the vapor-phase mole fractions of the ternary system are very much close to those of the binary (CO_2 + toluene) system at the same pressure and 298 K.

The $P-T$ trace for S-L-V-E at constant liquid-phase compositions is obtained from the isothermal plots of P versus $[x_3/(1 - x_3)]$ at three temperatures and is shown in Figure 7. It can be seen that the pressure required for attaining S-L-V-E 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.[5]

Finally, triangular-phase diagrams for the (CO_2 + toluene + naphthalene) system have been generated using this new method in order to demonstrate how the method can be utilized for selection of crystallization pathway in the SAS process. Figures 8 and 9 depict the effects of variations in pressure and temperature on isothermal and isobaric triangular-phase diagrams, respectively. It can be seen that the isothermal S-L-V region shrinks with in-

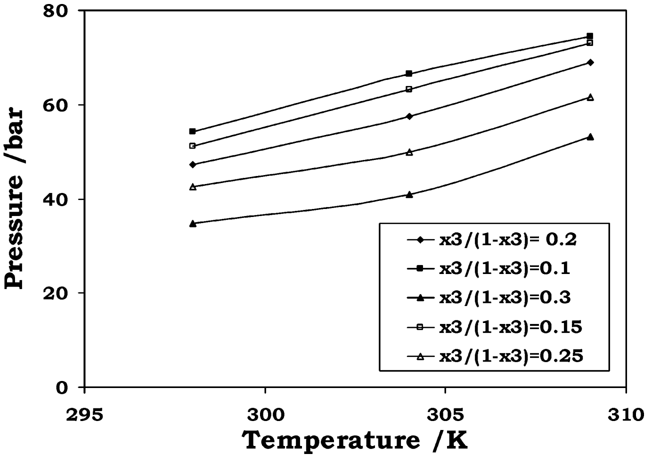

Figure 7. Effect of temperature on bubble point pressures (P-T trace) for naphthalene + toluene + CO_2 at S-L-V equilibrium.

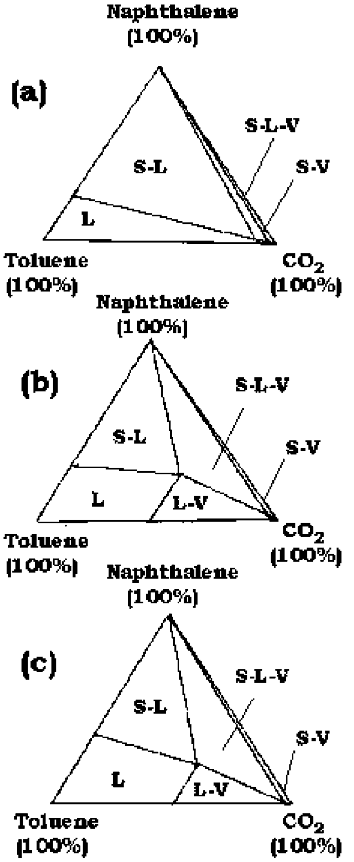

Figure 8. Effect of temperature on S-L-V region for 58.2 bar at (a) 298 K, (b) 304 K, and (c) 309 K.

creasing pressure and gets completely eliminated above the mixture critical pressure. This indicates that the solid crystallization pathway directly traverses from the S-L region to the S-V region above the mixture critical pressure, which is desirable for the solvent-free particles. However, the S-L-V region expands with increasing temperature, at a constant pressure.

Conclusion

The new prediction method for ternary S-L-V-E utilizes PMVF of the solvent in the binary (CO_2 + solvent) liquid mixture calculated by using the P-R EOS and the solid solubility at a reference pressure. PMVF of the solvent depicts the solvent power of the solvent diluted with CO_2 and is utilized for prediction of isothermal ternary S-L-E at different CO_2 mole fractions or pressures, prior to the usual ternary V-L-E calculations. This method has been demonstrated to yield good agreements of the experimental data with the corresponding calculated values of the bubble point pressures for two systems: (i) CO_2 + toluene + naphthalene and (ii) CO_2 + toluene + phenanthrene, in this paper. The method has been successful in predicting the *P*−*T* trace for S-L-V-E and the ternary-phase diagrams, which are needed to assess the S-L-V region for selecting the process conditions of the SAS process.

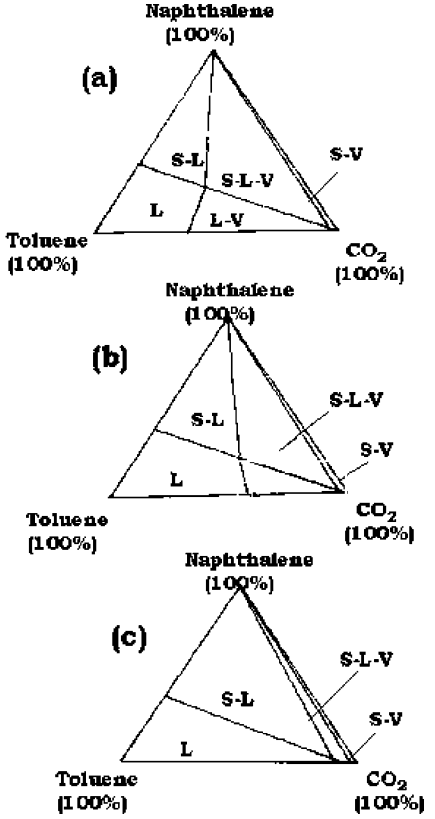

Figure 9. Effect of pressure on S-L-V region for 298 K at (a) 32.9 bar, (b) 43.4 bar, and (c) 57.7 bar.

Literature Cited

(1) Mukhopadhyay, M. Partial molar volume reduction of solvent for solute crystallization using carbon dioxide as antisolvent. *J. Supercrit. Fluids* **2003**, *25*, 213−223.

(2) Mukhopadhyay, M.; Dalvi, S. V. Solid solubility prediction from partial molar volume fraction of solvent in antisolvent−solvent mixture. In *Proceedings of SuperGreen−2002*, the First International Symposium on Supercritical Fluid Technology for Energy and Environmental Applications, Suwon, Korea, November 2002; pp 155−160.

(3) Mukhopadhyay, M.; Dalvi, S. V. Partial molar volume fraction of solvent in binary (CO_2−solvent) solution for solid solubility predictions. *J. Supercrit. Fluids* **2004**, *29*, 221−230.

(4) Dixon, D. J.; Johnston, K. P. Molecular thermodynamics of solubilities in gas antisolvent crystallization. *AIChE J.* **1991**, *37*, 1441−1449.

(5) Kikic, I.; Lora, M.; Bertucco, A. A thermodynamic analysis of three phase equilibria in binary and ternary systems for applications in rapid expansion of supercritical solution (RESS), particles from gas saturated solutions (PGSS) and supercritical antisolvent (SAS). *Ind. Eng. Chem. Res.* **1997**, *36*, 5507−5515.

(6) Prausnitz, M.; Lichtenhaler, R. N.; Gomez de Azevedo, E. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice Hall: Englewood Cliffs, NJ, 1999.

(7) Badilla, J. C. D. F.; Peters, C. J.; Arons, J. D. S. Volume expansion in relation to the gas antisolvent process. *J. Supercrit. Fluids* **2000**, *17*, 13−23.

(8) Shariati, A.; Peters, C. J. Measurements and modeling of the phase behavior of ternary systems of interest for the GAS

process: i. the system carbon dioxide + 1-propanol + salicylic acid. *J. Supercrit. Fluids* **2002**, *23*, 195−208.

(9) Chang, C. J.; Randolph, A. D. Solvent expansion and solute solubility predictions in gas-expanded liquids. *AIChE J.* **1990**, *36*, 939−942.

(10) Kikic, I.; Bertucco, A.; Lora, M. A thermodynamic description of systems involved in supercritical antisolvent processes. In *Proceedings of the Fourth International Symposium on Supercritical Fluids*; Perrut, M., Brunner, G., Eds.; 1997; Vol. 1, pp 39−42.

(11) Mukhopadhyay, M. *Natural Extracts Using Supercritical Carbon Dioxide*; CRC Press: Boca Raton, FL, 2000; Chapter 2.

(12) Kordikowski, A.; Schenk, A. P.; Nielen, R. M. V.; Peters, C. J. Volume expansions and V-L-E of binary mixtures of a variety of polar solvents and certain near critical solvents. *J. Supercrit. Fluids* **1995**, *8*, 205−216.

Received for review January 19, 2005. Accepted May 26, 2005.

JE050028W