Solid-Fluid Equilibria in Natural Gas Systems[1]

Amyn S. Teja[2,3], Vicky S. Smith[2] and Tongfan Sun[2]

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

[2] School of Chemical Engineering, Georgia Institute of Technology Atlanta, GA 30332-0100, U.S.A.

[3] To whom correspondence should be addressed.

Abstract

Solid-fluid equilibria (SFE) in natural gas systems were calculated using a number of equations of state (EOS) including the Redlich-Kwong-Soave (RKS) equation, the Peng-Robinson (PR) equation, the Patel-Teja (PT) equation, and a Lennard-Jones (LJ) equation of state. A variety of mixing rules were used with one of the equations of state to study the effect of the mixture model on calculations of SFE. The natural gas systems studied included n-alkanes in supercritical carbon dioxide and n-alkanes in ethane. The predictive capabilities of the equations were examined by extrapolating data to high pressures and temperatures where the extrapolations were compared with experimental results.

Keywords: solid-fluid-equilibria; equation of state, Patel-Teja equation; solid n-alkane solubility, supercritical, carbon dioxide, ethane.

Introduction

Pipeline plugging due to the deposition of heavy hydrocarbons from natural gas is a significant problem for the natural gas industry. In pumping, transporting, and storage of natural gas from offshore wells, large amounts of heavy hydrocarbons can precipitate in the pipelines leading to plugging, corrosion, and increased pumping requirements at the well-head [1]. A knowledge of solid solubilities of heavy hydrocarbons in natural gas components is therefore of practical importance. Such knowledge is also important from a theoretical perspective because it provides information on interactions between unlike molecules. Experimental data for SFE are scarce and, when available, can sometimes be inconsistent because accurate measurements are difficult to make. There is therefore a need for a reliable method of prediction of such equilibria in systems relevant to natural gas processing.

Common methods for SFE calculation include generalized equations of state, especially those of the van der Waals type [2-4] and expanded liquid models. Although equations of state have been successfully used to correlate multi-phase equilibria, they have distinct limitations when applied to solid-fluid mixtures of interest in this work. Attempts at overcoming some of these limitations have relied on improved mixing rules and several of these mixing rules have been compared in this work. Special attention was given to the PT equation [4] and a LJ equation [5] to test their capabilities for the correlation and prediction of SFE. Comparisons were made such that the capabilities of equations of state to describe SFE over a wide range of conditions could be evaluated. The results of these calculations are described below.

SFE Calculations

For a pure solid solute in equilibrium with a supercritical fluid phase, we may write [6]

$$P_2^S \varphi_2^S \exp\left\{ \int_{P_2^S}^{P} \frac{V_2^S}{RT} dP \right\} = y_2 \varphi_2^F P \qquad (1)$$

where P_2^S is the sublimation (vapor) pressure of the solute 2, φ_2^S is the fugacity coefficient of the solute at its sublimation pressure, V_2^S the molar volume of the solute, y_2 the composition (solubility) of the solute in the supercritical solvent, φ_2^F the fugacity coefficient of the solute in the supercritical solvent, and P is the pressure. All properties are evaluated at the system temperature. Since the sublimation pressure is usually very small, we may assume $\varphi_2^S \approx 1$ and the integral to be evaluated from zero pressure to the system pressure P. Also, since the solid molar volume is not significantly affected by pressure, we can integrate and rewrite Equation (11) as follows:

$$y_2 = \frac{P_2^S \exp\left[PV_2^S / RT\right]}{P\varphi_2^F} \tag{2}$$

Thus, if the solid-phase properties (density and sublimation pressure) are known, then the solubility of the solute in the supercritical solvent at any pressure and temperature can be calculated provided that an equation of state is available for the calculation of φ_2^F.

The fugacity coefficients φ_2^F can be calculated from the equation of state by:

$$RT \ln\left(\varphi_2^F\right) = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_2}\right)_{T,V,n_1} - \frac{RT}{V}\right] dV - RT \ln\left(\frac{PV}{nRT}\right) \tag{3}$$

where n_2 is number of moles of the solute, and V is the total volume of the fluid phase. In this work, analytical expressions for the fugacity coefficient were obtained for the cubic equations, but a numerical method was applied to the LJ equation.

Mixing Rules

Two kinds of van der Waals one-fluid mixing rules were used to extend the LJ and cubic equations to mixtures. The van der Waals (VW) rule for the LJ equation may be written as:

$$\sigma^3 = \Sigma\Sigma\, y_i\, y_j\, \sigma^3_{ij} \tag{4}$$

$$\varepsilon\, \sigma^3 = \Sigma\Sigma\, y_i\, y_j\, \varepsilon_{ij}\, \sigma^3_{ij}$$

with $\sigma_{12} = \sigma_{21} = 0.5\,(\sigma_1 + \sigma_2)\,(1 - L_{12})$

$$\varepsilon_{12} = \varepsilon_{21} = (\varepsilon_1 \varepsilon_2)^{0.5} (1 - L_{21})$$

where L_{12} and L_{21} are binary interaction coefficients.

For the cubic equations, the van der Waals mixing rules may be written

$$a = \Sigma\Sigma\, y_i\, y_j\, a_{ij}$$

(5)

$$b = \Sigma\, y_i\, b_i$$

$$c = \Sigma\, y_i\, c_i$$

with $a_{ij} = a_{ji} = (a_i\, a_j)^{0.5} (1 - K_1)$

$$b_{ij} = (b_i + b_j)(1 - K_2)$$

where K_1 and K_2 are binary interaction parameters. This mixing rule is denoted as VW1 when $K_1 \neq 0$, $K_2 = 0$, and VW2 when $K_1 \neq 0$, $K_2 \neq 0$.

Conventional mixing rules, such as the van der Waals one-fluid rules described above, are known to be inadequate for mixtures of molecules of greatly different size such as the mixtures studied in this work. Thus, activity coefficient based mixing rules were also used in this work. Incorporation of activity coefficient models into cubic equations such as the PT equation is accomplished by deriving an expression for the excess Helmholtz energy in terms of the mixture constants *a* and *b*. The excess Helmholtz energy expression for the PT equation of state at infinite pressure is:

$$A_{\infty}^{E} = \frac{a_m}{D_m} - \sum y_i \frac{a_i}{D_i} \qquad (6)$$

with $D_i = Q_i \,/\, \ln\left(\frac{3b_i + c_i - Q_i}{3b_i + c_i + Q_i}\right)$ and $Q_i = \sqrt{b_i^{\,2} + 6b_i c_i + c_i^{\,2}}$ (7)

where A^E is the excess Helmholtz energy at the infinite pressure limit and is obtained from activity coefficient models, and i can be 1, 2, ..., or m (mixture). It is known that $D_i = b_i / [2^{-0.5} \ln (2^{0.5} - 1)]$ for the PR equation.

Wong and Sandler [7] equated the excess Helmholtz energy at infinite pressure from an EOS with the excess Gibbs energy at low pressure from an activity coefficient model. In

addition, they constrained their equations to the low density virial limit with the following mixing rule (denoted as WS):

$$B = b - \frac{a}{RT} = \sum_i \sum_j y_i y_j \left(b - \frac{a}{RT} \right)_{ij} \tag{8}$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] \left(1 - K_{ij} \right)$$

where B is the second virial coefficient, and K_{ij} is an adjustable parameter obtained by matching low pressure excess Gibbs energy data. The "Wong-Sandler" equations are density-independent, preserving the cubic nature of the EOS and maintaining ease in computation.

Satyro and Trebble [8] pointed out that the Wong-Sandler mixing rules introduce a temperature dependence on the EOS constant *b*. As discussed by Trebble and Bishnoi [9], such a functionality could result in thermodynamically inconsistent results such as negative heat capacities at higher pressures. Satyro and Trebble [10] therefore modified the Wong-Sandler mixing rules to eliminate the inconsistency caused by the temperature dependence of the EOS constant *b*. Instead of a mixing rule based on the virial limit, equation 8 above, they proposed using the quadratic van der Waals one-fluid mixing rule (denoted as ST):

$$b = \sum_i \sum_j y_i y_j b_{ij} \qquad \text{and} \qquad b_{ij} = 0.5(b_i + b_j)(1 - k_{ij}) \tag{9}$$

where the term k_{ij} is calculated by matching the excess Gibbs energy calculated from the EOS to that calculated from the activity coefficient model. This modification is a departure from the inherent second virial boundary condition of the Wong-Sandler mixing rules.

Salim and Trebble [11] further modified the Wong-Sandler mixing rules to include the quadratic composition dependence of the second virial coefficient. They applied their mixing rules to three or four-constant cubic EOS. In order to avoid the thermodynamic inconsistency caused by a temperature-dependent EOS constant *b*, they added a volume dependent term to the attractive term of the EOS. The EOS for the mixture is therefore quartic in volume and the additional term, a^0, is evaluated at the infinite pressure limit of the EOS.

A method analogous to that of Salim and Trebble [11] was used to modify the Patel-Teja EOS as follows:

$$p = \frac{RT}{v-b} - \frac{a + a^0 / v}{v^2 + (b+c)v - bc} \tag{10}$$

with $$a^0 = 2b_m c_m \left(A_\infty^E - \frac{a_m}{b_m} + \sum_i y_i \frac{a_i}{D_i} \right) / \left(\ln 2 + \frac{b_m + c_m}{D_m} \right) \tag{11}$$

The term a^0 was evaluated at the infinite pressure limit of the modified PT EOS (MPT).

The NRTL model was chosen in this work to obtain A^E . This model is given by

$$\frac{g^E}{RT} = y_1 y_2 \left(\frac{\tau_{21} G_{21}}{y_1 + y_2 G_{21}} + \frac{\tau_{12} G_{12}}{y_2 + y_1 G_{12}} \right) \tag{12}$$

$$G_{12} = \exp(-0.3\,\tau_{12}) \quad \text{and} \quad G_{21} = \exp(-0.3\,\tau_{21}) \tag{13}$$

where g^E is the excess Gibbs energy, and τ_{12} and τ_{21} are adjustable parameters obtained by fitting experimental data.

Correlations of SFE

First we compared the ability of various equations of state to correlate SFE behavior over wide ranges of temperature and pressure. The equations of state studied were the LJ, RKS, PR, and PT equations. All equations were combined with the van der Waals mixing rule with two adjustable parameters (VW2). Sublimation pressures of the n-alkanes were obtained from the literature [12,13] and solid densities were supplied by the manufacturer. For the cubic equations of state, the critical temperature and pressure of long chain n-alkanes were calculated using the correlations developed by Teja et al. [14]. The acentric factors were estimated from the correlation of Han and Peng [15]. The LJ size and energy constants of long chain n-alkanes were estimated by extrapolation of the correlation for methane to hexanedecane given by Sun and Teja [5]. All these properties are given in Table 1.

The calculated results for each model are given in Table 2 where the average absolute deviations between experimental and calculated solubilities are reported. The

AAD is rather large in most cases because of scatter in the experimental data. It shows that, among the cubic equations studied, the PT equation is probably the best for correlating data. Therefore we chose the PT equation for further examination and comparisons with the LJ equation.

Three activity coefficient mixing rules were used with the PTEOS for additional comparisons. The mixture models included the Wong and Sandler mixing rule, the Satyro and Trebble mixing rule, and the Salim and Trebble modified cubic equation + mixing rule. These (when combined with the NRTL model) are denoted by PT+WS, PT+ST, and MPT+WS in the tables. Since solid solubilities of alkanes in natural gas components are very small (y_2 of the order of 10^{-4}), a strong correlation between τ_{12} and τ_{21} was observed. Therefore, τ_{21} was set equal to 1 throughout the calculations, and only two adjustable parameters (K_{ij} and τ_{12}) were used in the calculations. Results of the calculations are reported in Table 3. It can be seen that the LJEOS, MPT+WS and PT+VW2 are better than the other models in correlating solubility data. These models were therefore chosen for additional comparison of the predictive capabilities of the models.

SFE Predictions

The predictive capability of the models was examined by extrapolating SFE data over significant ranges of temperature and pressure. The temperature extrapolation capability of the three models was tested using the n-C_{28} + CO_2 system. The results are shown in Figure 1 where there are nine sets of experimental data from T=308.0 to 325.2 K, and there are three model predictions at 5 temperatures T=325.2, 323.4, 318.1, 313.1, and 308.1 K. The predictions were made using interaction coefficients obtained at T=318.6 K. The PT+VW2 and MPT+WS models over-predict the temperature effect on solubilities -- the predictions are too high at T=352 K, but too low at T=308.1 K. The PT+ST predictions are too low at T=325 and 323 K.

Pressure extrapolations were studied in the n-C_{28} + CO_2 system at T=325.2 K. Six predictions are given in Figure 2 where the curves were calculated using fitted data at

pressures from 120 to 200 bar containing 10 data points. It is seen that the LJ model is the best in the pressure prediction while the PT equation predictions are not accurate.

Summary

The LJEOS with the van der Waals one fluid model appears to adequately correlate and predict SFE behavior of solid n-alkanes in supercritical carbon dioxide and ethane. Cubic equations are generally adequate for correlating experimental data, but are inadequate for predicting data. All mixing rules tested appear to give comparable results for both correlation and prediction, provided the same number of adjustable parameters is used in the calculations.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Gas Research Institute and the Gas Processors Association for this work.

References

1. N.F. Carnahan, J. Petro. Tech. 41 (1989) 1024.
2. G. Soave, Chem. Eng. Sci., 27 (1972) 1197.
3. D.Y. Peng, and D.B. Robinson, Eng. Chem. Fundam., 15 (1976) 59.
4. N.C. Patel, and A.S. Teja, Chem. Eng. Sci., 37 (1982) 463.
5. T.F. Sun, and A.S. Teja, J. Phys. Chem., 100 (1996) 17365.
6. J.M. Prausnitz, R.N. Lichtenthaler, and G.E. De Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice Hall, Englewood-Cliffs, NJ. (1986).
7. D.S.H. Wong, and S.I. Sandler, AIChE J., 38 (1992) 671.
8. M.A. Satyro, and M.A. Trebble, Fluid Phase Equil., 115 (1995) 135.
9. M.A. Trebble, and P.R. Bishnoi, Fluid Phase Equil., 29 (1986) 465.
10. M.A. Satyro, and M.A. Trebble, Fluid Phase Equil., in press.
11. P.H. Salim, and M.A. Trebble, Ind. Eng. Chem. Res., 34 (1995) 3112.
12. I. Moradinia, and A.S. Teja, Fluid Phase Equil., 28 (1986) 199.
13. I. Moradinia, and A.S. Teja, J. Chem. Eng. Data, 33 (1988) 240.
14. A.S. Teja, R.J. Lee, D. Rosenthal, and M. Anselme, Fluid Phase Equil., 56 (1990) 153.
15. B. Han, and D.Y. Peng, Can. J. Chem. Eng., 71(1993) 332.
16. D. Ambrose, and C. Tsonopoulos, J. Chem. Eng. Data, 40 (1995) 531.
17. T.E. Daubert, and R.P. Danner, Data Compilation Table of Properties of Pure Compounds, Design Institute for Physical Properties Data, American Institute of Chemical Engineering, New York, N. Y. (1985).
18. V.S. Smith, P.O. Campbell, V. Vandana, and A.S. Teja, Intl. J. of Thermophys. 17 (1996)
19. D. Suleiman, Measurement and Prediction of Phase Equilibrium Properties at Infinite Dilution: Alkanes in Natural Gases and Organic Solvents in Aqueous Solution. Ph. D. Thesis, Georgia Institute of Technology, Atlanta, Georgia (1994).
20. M.A. McHugh, A.J. Seckner, and T.J. Yogan, Am. Chem. Soc., 23 (1984) 493.

21. E. Reverchon, P. Russo, and A. Stassi, J. Chem. Eng. Data, 38 (1993) 458.

Figure Captions

Fig. 1 Predictions of SFE in CO_2 + n-$C_{28}H_{58}$. The figure shows four sets of predictions at T=325.2, 323.4, 318.1 313.1, and 308.1 K corresponding to the points denoted by empty symbols using interaction coefficients obtained at T=318.6 K.

Fig. 2 Predictions of SFE in CO_2 + n-$C_{28}H_{58}$ at 325.2 K. Adjustable parameters were obtained by fitting 10 data points at pressures from 120 to 200 bar.

Table 1. Critical properties, acentric factors and LJ parameters used in this work

Substance	T_C(K)	P_C (bar)	ω	v^s (dm^3/mol)	σ (Å)	ε_0/k (K)	$\varepsilon_1/k(K)^{0.5}$
C_2H_6	305.32	48.72	0.0990		4.2431	289.23	-2.834
CO_2	304.19	73.82	0.2276		3.6514	356.25	-6.681
$C_{24}H_{50}$	809.96	10.496	1.032	0.424	9.226	2020	-48.1
$C_{25}H_{52}$	818.56	10.256	1.066	0.440	9.363	2087	-49.9
$C_{28}H_{58}$	842.11	9.694	1.163	0.489	9.755	2287	-55.5
$C_{29}H_{60}$	849.29	9.549	1.195	0.506	9.880	2352	-57.3
$C_{30}H_{60}$	856.17	9.421	1.226	0.522	10.003	2417	-59.2
$C_{32}H_{66}$	869.12	9.208	1.287	0.555	10.242	2546	-62.8
$C_{33}H_{68}$	875.22	9.119	1.317	0.571	10.358	2609	-64.6

T_C and P_C are obtained from Ambrose and Tsonopoulos [16] for n-alkanes up to C_{16}, Teja et al. [14] for n-alkanes > C_{16}, and Daubert and Danner [17] for CO_2.
ω obtained from Han and Peng [15] for n-alkanes > C_{16}, and Daubert and Danner (1985) for others.
The LJEOS was applied to real fluids by introducing effective LJ potential parameters σ and ε, with the ε being temperature dependent so that $\varepsilon = \varepsilon_o + \varepsilon_1 T^{0.5}$ [5].

Table 2. SFE calculations with various equations of state

			PT+VW1		RKS+VW2			PR+VW2			PT+VW2			LJ+VW		
Sul.	T(K)	Pts	K_1	AAD	K_1	K_2	AAD	K_1	K_2	AAD	K_1	K_2	AAD	L_{12}	L_{21}	AAD
Solvent: CO_2																
C24 [a]	310.0	11	0.003	16.2	0.174	0.333	16.0	0.118	0.267	14.0	0.028	0.114	11.2	-0.115	0.469	9.0
C25 [a]	308.0	4	0.027	40.8	0.236	0.467	8.6	0.184	0.438	10.0	0.099	0.347	12.2	-0.068	0.466	13.1
C28 [b]	325.2	16	-0.009	6.6	0.148	0.261	7.3	0.095	0.202	5.5	0.006	0.065	3.7	-0.124	0.495	4.9
C28 [a]	325.0	8	-0.010	5.1	0.157	0.297	1.9	0.107	0.257	1.6	0.021	0.149	1.1	-0.110	0.487	1.2
C28 [b]	323.4	11	-0.010	5.5	0.151	0.274	7.5	0.096	0.212	5.4	0.004	0.066	2.6	-0.123	0.495	3.2
C28 [b]	318.6	8	-0.012	4.2	0.144	0.253	9.2	0.088	0.185	7.4	-0.007	0.026	3.4	-0.128	0.497	3.3
C28 [c]	318.1	9	-0.010	54.4	0.189	0.408	8.6	0.136	0.368	7.8	0.046	0.267	13.5	-0.084	0.477	12.6
C28 [a]	318.0	6	-0.013	11.1	0.165	0.328	7.1	0.112	0.285	6.4	0.025	0.178	5.0	-0.101	0.484	4.8
C28 [c]	313.1	10	-0.012	20.0	0.170	0.340	28.1	0.112	0.278	25.5	0.014	0.122	18.5	-0.108	0.489	12.4
C28 [c]	308.1	8	-0.019	12.1	0.138	0.243	17.8	0.084	0.188	15.8	-0.011	0.042	11.9	-0.116	0.491	7.6
C28 [a]	308.0	11	-0.015	15.6	0.178	0.369	10.1	0.118	0.308	9.9	0.015	0.142	9.3	-0.103	0.486	8.6
C29 [a]	308.0	6	0.028	60.9	0.399	1.007	32.2	0.335	1.001	31.8	0.225	0.937	31.0	0.071	0.409	30.5
C30 [c]	320.0	5	-0.078	13.3	0.053	0.119	19.0	0.005	0.092	16.1	-0.084	-0.025	11.1	-0.129	0.482	12.4
Average				20.4			13.3			12.1			10.3			9.5
Solvent: C_2H_6																
C28 [d]	308.1	6	-0.117	22.8	0.026	0.169	21.0	-0.006	0.190	18.3	-0.089	0.111	16.8	-0.090	0.352	14.7
C29 [e]	308.1	5	-0.077	20.3	0.046	0.090	19.0	0.016	0.123	19.0	-0.065	0.048	18.7	-0.098	0.387	15.6
C30 [d]	308.1	6	-0.109	28.4	0.001	0.087	22.2	-0.048	0.024	21.0	-0.157	-0.224	19.1	-0.121	0.389	15.8
C30 [d]	313.1	4	-0.114	30.5	-0.038	-0.072	27.0	-0.079	-0.111	26.3	-0.172	-0.296	23.9	-0.133	0.396	18.0
C32 [d]	308.1	6	-0.125	35.0	-0.029	0.015	21.9	-0.083	-0.067	20.8	-0.200	-0.362	18.7	-0.133	0.404	14.3
C32 [d]	313.1	6	-0.117	42.3	-0.059	-0.125	20.2	-0.111	-0.218	18.8	-0.226	-0.526	15.4	-0.157	0.422	9.6
C32 [d]	319.1	4	-0.120	38.5	-0.111	-0.371	31.7	-0.154	-0.455	31.2	-0.250	-0.703	29.3	-0.181	0.439	25.9
C33 [e]	308.1	6	-0.079	34.0	0.028	0.047	20.9	-0.026	-0.029	19.5	-0.145	-0.318	17.2	-0.125	0.427	13.5
C33 [e]	313.1	6	-0.072	36.8	0.020	-0.007	21.0	-0.032	-0.080	19.2	-0.145	-0.352	15.8	-0.132	0.434	10.8
C33 [e]	318.1	4	-0.079	34.0	-0.007	-0.123	30.9	-0.048	-0.159	30.5	-0.140	-0.327	28.8	-0.132	0.435	25.2
Average				32.3			23.6			22.5			20.4			16.3

[a] Smith et al. [18] and Suleiman [19]. [b] McHugh et al. [20]. [c] Reverchon et al. [21].

[d] Moradinia and Teja [12]. [e] Moradinia and Teja [13].

Table 3. SFE calculations using the PT EOS with activity coefficient based mixing rules.

			PT+ST			PT+WS			MPT+WS		
Sul.	T(K)	Pts	K_{ij}	τ_{12}	AAD	K_{ij}	τ_{12}	AAD	K_{ij}	τ_{12}	AAD
					Solvent: CO_2						
C24 [a]	310.0	11	0.062	7.495	11.1	0.853	7.547	11.2	0.854	6.584	12.0
C25 [a]	308.0	4	0.187	7.497	12.6	0.867	7.615	12.5	0.872	4.500	10.8
C28 [b]	325.2	16	0.049	7.062	3.8	0.868	7.192	3.8	0.869	6.356	3.9
C28 [a]	325.0	8	0.103	5.863	1.4	0.870	6.100	1.5	0.871	4.524	1.6
C28 [b]	323.4	11	0.045	7.149	2.8	0.868	7.244	2.8	0.868	6.450	2.8
C28 [b]	318.6	8	0.017	7.791	3.3	0.866	7.826	3.5	0.866	7.561	3.6
C28 [c]	318.1	9	0.144	5.612	13.4	0.871	5.704	13.3	0.874	3.005	10.1
C28 [a]	318.0	6	0.098	6.231	5.0	0.869	6.313	5.0	0.871	4.691	5.5
C28 [c]	313.1	10	0.063	7.258	18.3	0.867	7.274	18.4	0.868	6.063	19.5
C28 [c]	308.1	8	0.022	7.664	11.7	0.863	7.680	11.7	0.864	7.465	11.8
C28 [a]	308.0	11	0.072	7.089	9.4	0.866	7.104	9.4	0.868	5.761	9.9
C29 [a]	308.0	6	0.473	3.335	31.0	0.894	3.367	31.0	0.907	-7.008	33.0
C30 [c]	320.0	5	0.020	1.661	11.1	0.862	1.933	11.3	0.861	1.968	11.2
Average					10.4			10.4			10.4
					Solvent: C_2H_6						
C28 [d]	308.1	6	-0.085	-4.813	16.0	0.808	-5.167	15.5	0.809	-5.204	15.9
C29 [e]	308.1	5	-0.057	-2.699	18.3	0.820	-2.954	18.2	0.821	-2.916	18.4
C30 [d]	308.1	6	-0.168	-4.615	18.8	0.812	-4.784	18.3	0.807	-2.424	17.2
C30 [d]	313.1	4	-0.237	-3.639	23.1	0.809	-4.067	22.6	0.806	-1.879	21.6
C32 [d]	308.1	6	-0.229	-5.667	18.5	0.813	-5.818	18.0	0.806	-1.972	15.9
C32 [d]	313.1	6	-0.313	-4.072	16.0	0.811	-4.243	15.0	0.802	0.824	11.0
C32 [d]	319.1	4	-0.422	-1.952	28.9	0.809	-2.345	28.6	0.801	2.811	26.5
C33 [e]	308.1	6	-0.192	-2.439	17.1	0.826	-2.540	16.7	0.820	0.744	14.7
C33 [e]	313.1	6	-0.214	-1.640	15.8	0.826	-1.763	15.2	0.821	1.597	12.8
C33 [e]	318.1	4	-0.223	-1.325	28.1	0.827	-1.644	28.0	0.824	0.652	27.2
Average					20.1			19.6			18.1

[a-e] See the footnotes of Table 2.

Fig 1

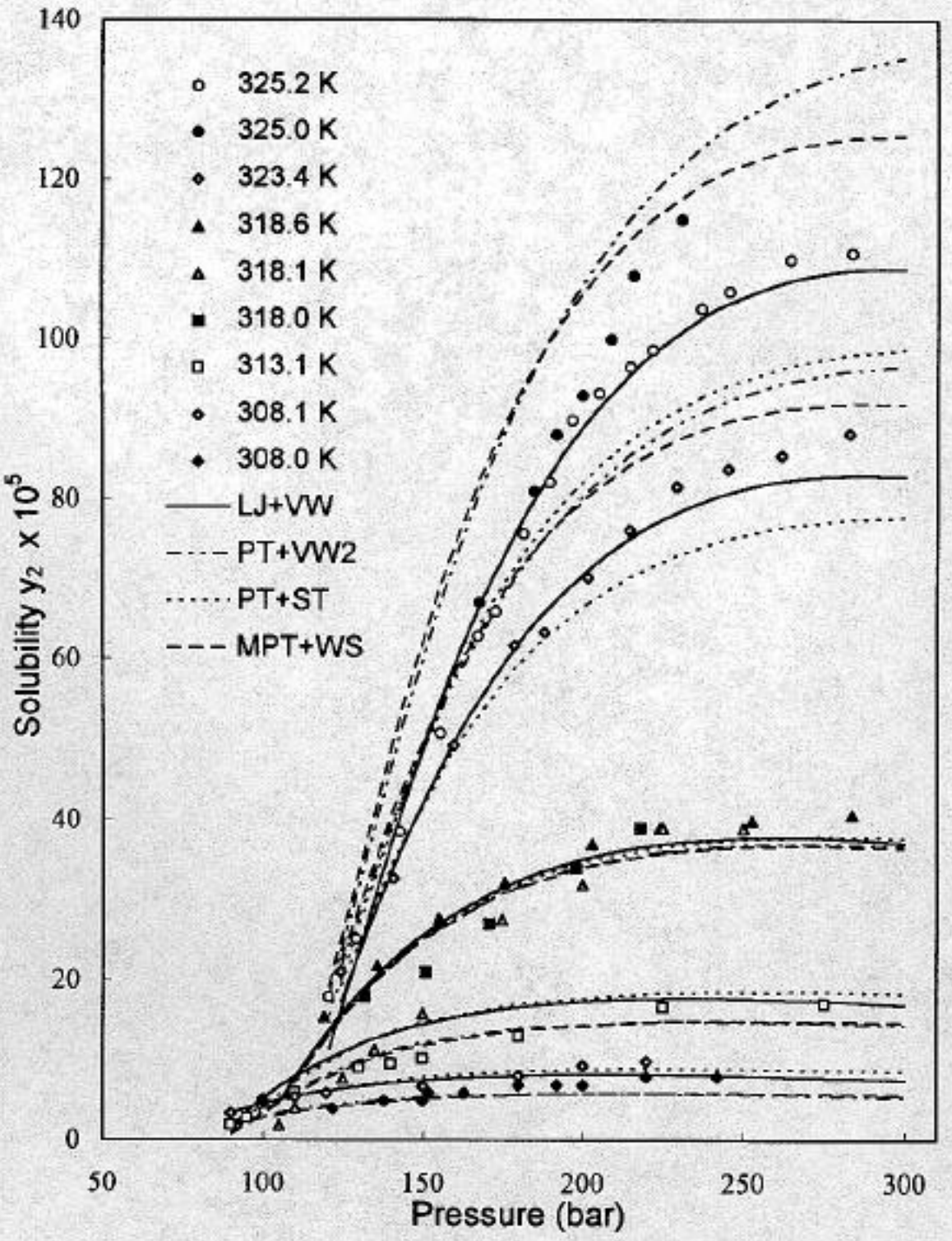
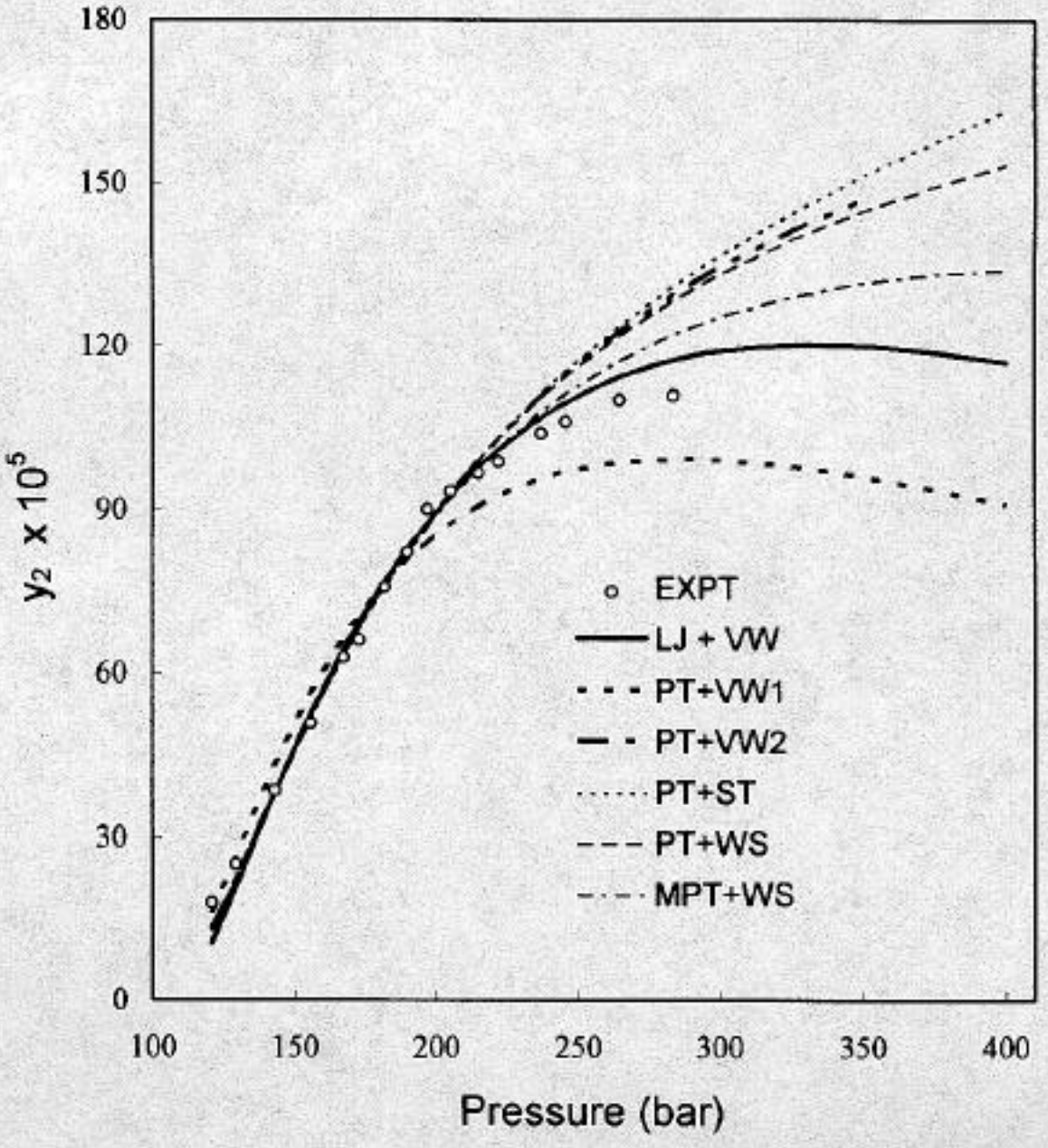

325.2 K
325.0 K
323.4 K
318.6 K
318.1 K
318.0 K
313.1 K
308.1 K
308.0 K
LJ+VW
PT+VW2
PT+ST
MPT+WS
Solubility $y_2 \times 10^5$
Pressure (bar)
0
20
40
60
80
100
120
140
50
100
150
200
250
300

Fig 2


180
150
120
90
60
30
0
100
150
200
250
300
350
400
$y_2 \times 10^5$
Pressure (bar)
EXPT
LJ + VW
PT+VW1
PT+VW2
PT+ST
PT+WS
MPT+WS