INVESTIGATION OF THE PHASE BEHAVIOUR OF PURE SOLIDS OR BINARY SOLID MIXTURES IN SUPERCRITICAL CARBON DIOXIDE

Michael Türk*, Martin Steurenthaler, Gerd Upper

Institut für Technische Thermodynamik und Kältetechnik, Universität Karlsruhe (TH)
*Corresponding author. Tel.: + 49 721 608 2330; fax: + 49 721 608 2335
Email: mt@ttk.uni-karlsruhe.de

Over the last few decades, various particle formation processes (e.g. GAS, PGSS and RESS) have been investigated extensively. Among others, one of the key properties in such processes is the solubility of pure solids or binary solid mixtures in supercritical fluids. In case of the RESS-process, an insufficient solubility limits the practical application. Moreover, the phase behaviour – especially the solid-liquid-gas three-phase-line (SLG-line) of the systems involved – has to be known, at least qualitatively. It was shown in previous investigations, that the product properties (e.g. particle size and morphology) - of the particles produced by RESS are often strongly influenced by the underlying phase behaviour. Thus, such information forms an important part of establishing the feasibility of any particle formation process. Therefore, the SLG-line of the binary systems CO_2 / benzoic acid, CO_2 / Phytosterol, CO_2 / L-polylactic acid and of the ternary system CO_2 / L-polylactic acid / Phytosterol have been investigated. The experiments were carried out in a static equilibrium apparatus, which allows a visual determination of the SLG-line following the first melting point method. In the second part of the present paper, we compare different cubic equations of state for the correlation and reliable prediction of the solid-liquid-gas as well as the solid-gas equilibrium. Moreover, it will be demonstrated that the SLG-line can be represented by the Redlich-Kwong-Soave and by the Peng-Robinson equation of state with binary interaction parameters fitted to the p-T trace of the SLG-line. Furthermore, the use of these binary interaction parameters enables an adequate thermodynamic modelling for the representation of the solubility of low volatile substances in supercritical fluids.

1. INTRODUCTION

In recent years, there has been a growing interest in the formation of small particles of low volatile organic substances using supercritical fluids. Usually, in such processes mixtures composed of one solute of low volatility differing appreciably from the supercritical solvent in mass, size, interaction strength, polarity, and shape are involved. These highly asymmetric binary mixtures have interesting properties because of the different behaviours of the components. Until now, there are several methods for the formation of small low volatile organic substances. The primary techniques for particle formation involving supercritical fluids are: RESS (Rapid Expansion of Supercritical Solutions), PGSS (Particle Generation from Gas Saturated Solution), and GAS (Gas Anti-Solvent). Among others, one of the key properties in such processes is the solubility of the low volatile substance in the supercritical fluid. Moreover, the phase behaviour – especially the solid-liquid-gas three-phase-line (SLG-line) of the mixtures involved – has to be known at least qualitatively. It was shown in literature, that the product properties (e.g. particle size and morphology) of the particles produced by RESS are often strongly influenced by the underlying phase behaviour [1,2]. In order to overcome the lack of reliable phase equilibrium data, experimental investigations

have been carried out in a static equilibrium apparatus. However, since reliable measurements of the phase behaviour of low volatile substances and supercritical fluids is time consuming and the cost of these measurements is quite high there is a need for reducing the experimental work by applying a suitable equation of state. Thus, one aim of our current activities is to evaluate and to compare different cubic equations of state for the correlation and reliable prediction of the solid – liquid - gas as well as the solid - gas equilibrium. Among others, the following systems have been investigated: CO_2 / benzoic acid, He / benzoic acid, CO_2 / biphenyl, He / biphenyl, CO_2 / Phytosterol, CO_2 / L-polylactic acid and the ternary system CO_2 / L-polylactic acid / Phytosterol. In this paper, it will be demonstrated that the SLG-line can be represented by the Redlich-Kwong-Soave (RKS) and by the Peng-Robinson (PR) equation of state (EoS) with the van der Waals mixing and combination rules fitted to the p-T trace of the SLG-line. From an engineering point of view, these EoS are able to predict the solid - fluid-, the vapour - liquid-, and the solid - liquid - gas - equilibrium of supercritical mixtures reasonably well. Furthermore, it is shown that the use of these binary interaction parameters enables an adequate thermodynamic modelling of the phase behaviour of low volatile substances in supercritical fluids.

2. EQUATIONS OF STATE

For the description of the experimental results of the SLG-data various cubic equations of state were used. These equations of state can be written as follows:

$$p = \frac{R \times T}{(v - b)} - \frac{a(T)}{v^2 + v \times (b + c) - (b \times c + d^2)} \tag{1}$$

with $d = c = 0$ for the RKS-EoS and $c = b$ and $d = 0$ for the PR-EoS [3,4]. In Eq. (1), where p is the pressure, T the temperature, v the molar volume, R = 8.31451 J mol^{-1}K^{-1} the gas constant, only the parameter $a(T) = a_C \times \alpha(T)$ is treated as a function of temperature. The temperature dependence of the attraction parameter $\alpha(T)$ was represented using the equations proposed by the authors in the original publications. The cubic equations of state represented by Eq. (1) where applied to the binary systems using the classical van der Waals (vdW) mixing and combination rules:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \cdot a_{ij} \qquad \text{with} \quad a_{ij} = a_{ji} = \sqrt{a_i \cdot a_j} \cdot \left(1 - k_{ij}\right) \tag{2a}$$

$$b = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \cdot b_{ij} \qquad \text{with} \quad b_{ij} = b_{ji} = \frac{b_i + b_j}{2} \cdot \left(1 - l_{ij}\right) \tag{2b}$$

The SLG-line can be calculated by solving Eq. (3) - (5) simultaneously, where f is the fugacity calculated by the cubic equations of state. Due to the fact, that the solid state of a pure substance cannot be represented by a conventional equation of state, it is assumed that the fugacity of the pure solid at given pressure and temperature can be related to a sub-cooled liquid reference state [5,6]. In Eq. (6), where Δh_i^{fus} is the heat of fusion and T_i^{fus} the temperature of fusion of the pure substance, the second term on the right side considers the pressure dependence. Of course, this expression neglects minor terms, which are a function of differences in heat capacities [5,6]. For the substances investigated, the physico-chemical

properties were taken from Schmitt and Reid or were calculated with contribution group methods respectively [7,8].

$$f_k^G(T,p,y) = f_k^L(T,p,x) \tag{3}$$

$$f_i^G(T,p,y) = f_i^L(T,p,x) \tag{4}$$

$$f_{i,0}^S(T,p) = f_i^G(T,p,y) \tag{5}$$

$$\ln \frac{f_{i,0}^S}{f_{i,0}^L} = \left[\frac{\Delta h_i^{fus}}{R \times T_i^{fus}} \left(1 - \frac{T_i^{fus}}{T}\right) + \int_{p_0}^{p} \frac{v_{i,0}^S - v_{i,0}^L}{R \times T} \ dp \right] \tag{6}$$

3. RESULTS AND DISCUSSION

As the SLG-line depends strongly on the solubility of the supercritical solvent in the melt of the organic solute, the melting point depression can be manipulated by changing the supercritical solvent or by using supercritical solvent mixtures. Among others, the following binary systems have been considered: CO_2 / benzoic acid, He / benzoic acid, CO_2 / biphenyl, He / biphenyl, CO_2 / Phytosterol, CO_2 / L-polylactic acid and the ternary system CO_2 / L-polylactic acid / Phytosterol. For these systems, experimental data for the melting points under high pressures could be obtained from literature [9-12] or were measured by our group. The experimentally determined three phase SLG-lines are listed in Table 1.

First of all, in order to prove the reliability of our measurement technique, the SLG-line of the binary system CO_2 / benzoic acid was determined and the results were compared with data published by Wilken and Gmehling [9]. These authors used the scanning transitiometry for the determination of the thermal properties instead of the first melting point method. Although different measurement techniques were applied, it can be seen in Figure 1 that both data sets are in good agreement with each other. The SLG-line of the systems CO_2 / benzoic acid and He / benzoic acid can be described by the RKS-EoS and the PR-EoS acceptably well in such a way that no difference can be noticed between both correlations. For the melting point of biphenyl in the presence of CO_2, the RKS-EoS yields to a better description than the PR-EoS, especially at higher pressures whereas no remarkable difference between the two equations of state is obvious in case of the presence of He. The calculations were performed using one binary interaction parameter in the attraction term (k_{ij}) with the exception of the CO_2 / biphenyl system where a second parameter was introduced in the repulsion term (l_{ij}).

Figure 2 shows solubility data for benzoic acid in carbon dioxide at 308 K and 328 K. Beside the experimental data, the slope of the solubility versus pressure isotherm calculated by the RKS-EoS and the PR-EoS is depicted. Although the binary interaction parameters were fitted exclusively to the SLG-data a good representation of the experimental solubility data was achieved, whereas the PR-EoS agrees better with the experimental data at higher pressures. For a better comparison of the quality of the prediction, the RKS-EoS and the PR-EoS were fitted to the solubility data of benzoic acid in carbon dioxide, too. Due to the fact that there is nearly no difference between the solubility calculated with the RKS-EoS and the PR-EoS, only the RKS-EoS (SG) is shown in Figure 2.

For the CO_2 / Phytosterol system Figure 3 shows that the PR-EoS describes the SLG-line slightly better than the RKS-EoS. In case of the systems involving L-polylactic acid no satisfying correlation with cubic equations of state could be achieved until now. Nevertheless,

it is worth to point out that the melting point depression of the mixture consisting of 50 mol-% L-polylactic acid and 50 mol-% Phytosterol in the presence of carbon dioxide is about 59 K instead of about 50 K for the system CO_2 / L-polylactic.

Table 1: Experimental data of the SLG-line for the systems investigated.

CO_2 / Phytosterol		CO_2 / L-polylactic acid	
p [MPa]	T [K]	p [MPa]	T [K]
0.10	413.2	0.10	404.3
3.11	404.0	3.36	393.6
6.31	398.6	7.11	383.6
8.64	393.8	11.27	373.5
11.54	388.7	13.33	368.6
15.13	383.6	18.14	358.7
18.83	378.5	22.17	353.4
25.14	373.5		

CO_2 / L-polylactic acid / Phytosterol		CO_2 / benzoic acid	
p [MPa]	T [K]	p [MPa]	T [K]
0.10	402.2	7.72	383.7
3.51	383.6	7.80	383.9
7.60	373.5	10.27	380.2
9.12	368.5	10.28	380.1
11.26	358.5	12.23	377.2
14.12	348.4	12.24	377.3
25.23	343.6	12.92	376.1
17.09	343.4	12.93	376.2
20.28	343.7	13.23	376.1
		14.91	374.5
		15.95	373.2
		16.15	373.2

4. CONCLUSIONS
Three phase SLG-data were experimentally determined for the systems CO_2 / benzoic acid, CO_2 / Phytosterol, CO_2 / L-polylactic acid and the ternary system CO_2 / L-polylactic acid / Phytosterol. These experimental melting points are represented by the RKS- and the PR-EoS using binary interaction parameters fitted exclusively to the p-T trace of the SLG-line. From an engineering point of view, these EoS are able to predict the solid - fluid-, the vapour - liquid-, and the solid - liquid - gas - equilibrium of supercritical mixtures reasonably well.
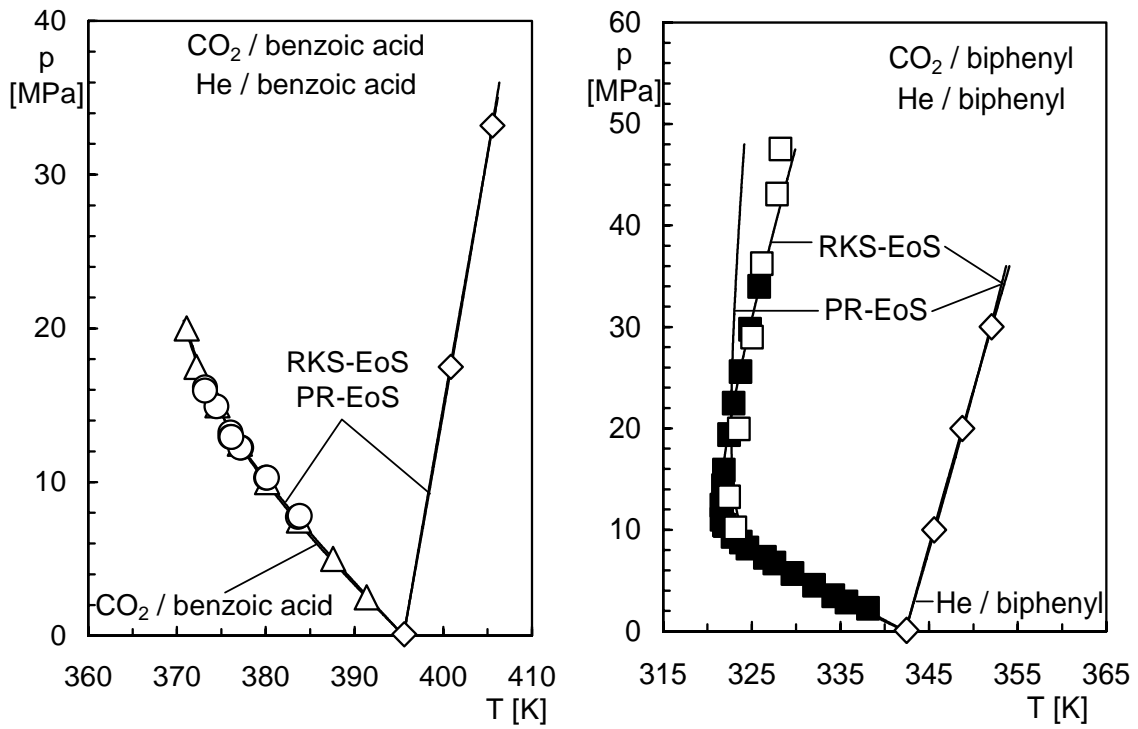
Figure 1: Melting points of benzoic acid and biphenyl in the presence of carbon dioxide or helium, $\bigcirc$ [this work], $\triangle$ [9], $\diamondsuit$ [10], $\blacksquare$ [11], $\square$ [12]; RKS-EoS and PR-EoS: fitted to SLG-data.
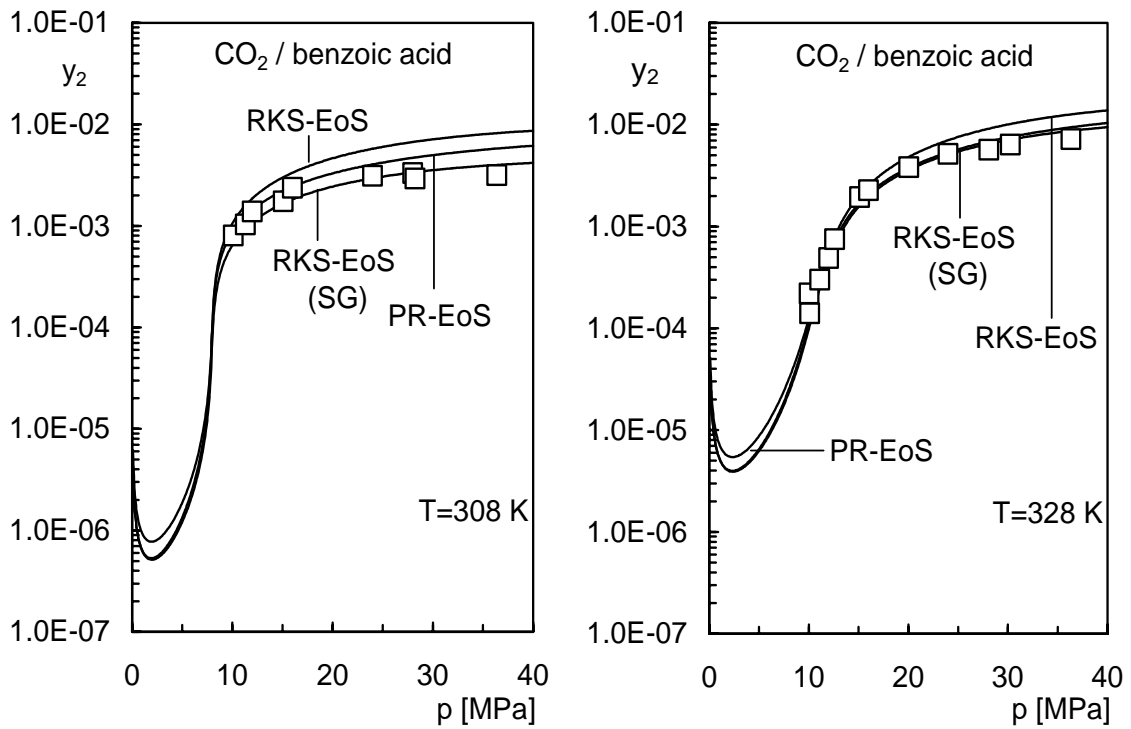

Figure 2: Solubility of benzoic acid in carbon dioxide at 308 K and 328 K [7]; RKS-EoS (SG): fitted to solubility data, RKS-EoS and PR-EoS: fitted to SLG-data.
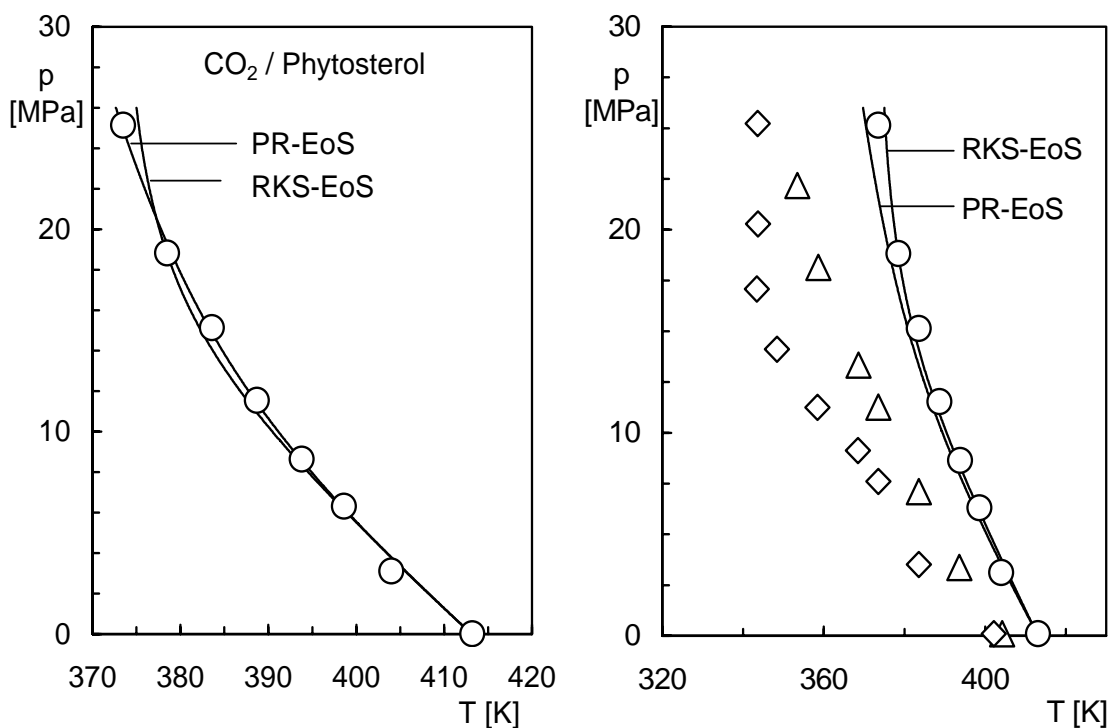
Figure 3: Melting points of Phytosterol, of L-polylactic acid, and of the binary system L-polylactic acid / Phytosterol in the presence of carbon dioxide, O Phytosterol, △ L-polylactic acid, ◇ L-polylactic acid / Phytosterol; RKS-EoS and PR-EoS: fitted to SLG-data.

6. REVERENCES

[1]   A. Diefenbacher, M. Türk, J. Supercrit. Fluids, 22 (2002) 175.
[2]   M. Türk, G. Upper: Phase behaviour of low volatile substances and supercritical fluids with regard to particle formation processes; Proceedings of the 20th European Symposium on Applied Thermodynamics (ESAT-2003), Lahnstein, Germany, October 9 - 12, 2003, 249.
[3]   D.Y. Peng, D.B. Robinson, Ind. Eng. Chem. Fundam., 15 (1976) 59.
[4]   G. Soave, Chem. Eng. Sci., 27 (1972) 1197.
[5]   J.M. Prausnitz, R.N. Lichtenthaler, E. Gomez de Azevedo, Molecular Thermodynamics of Fluid Phase Equilibria, Prentice-Hall, Englewood Cliffs, (1999).
[6]   I. Kikic, M. Lora, A. Bertucco, Ind. Eng. Chem. Res., 36 (1997) 5507.
[7]   W.J. Schmitt, R.C. Reid, Chem. Eng. Data, 31 (1986) 204.
[8]   R.C. Reid, J.M. Prausnitz, B.E. Poling, The properties of gases and liquids 4. ed., McGraw-Hill New York, (1987)
[9]   M. Wilken, J. Gmehling, Chemie Ingenieur Technik, 73 (2001) 1300.
[10] K. Fischer, M. Wilken, J. Gmehling, Fluid Phase Equilibria, 210 (2003) 199.
[11] P.L. Cheong et al., Fluid Phase Equilibria, 29 (1986) 555.
[12] M.A. McHugh, T.J. Yogan, J. Chem. Eng. Data, 29 (1984) 112.