INVESTIGATION OF THE PHASE BEHAVIOUR OF LOW VOLATILE SUBSTANCES AND SUPERCRITICAL FLUIDS WITH REGARD TO PARTICLE FORMATION PROCESSES

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ABSTRACT

In recent years, there has been a growing interest in the formation of small particles of low volatile substances using supercritical fluids. The most important techniques are GAS (Gas Anti-Solvent), PGSS (Particle Generation from Gas Saturated Solution) and RESS (Rapid Expansion of Supercritical Solutions). Among others, one of the key properties in such processes is the solubility of the low volatile substance in the supercritical fluid. 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 strongly influenced by the underlying phase behaviour. However, since reliable measurements of the phase behaviour of low volatile substances and supercritical fluids are 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, the aim of the current investigation 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. In the present paper, it will be shown that the SLG-line can be represented by the Redlich-Kwong-Soave-, (RKS-), and by the Peng-Robinson-, (PR-), Equation of State (EoS) with binary interaction parameters fitted to the pressure and the temperature at the UCEP (Upper Critical End Point) exclusively. Furthermore, the use of these binary interaction parameters enables an adequate thermodynamic model for the representation of the solubility as well as the partial molar volume of low volatile substances in supercritical fluids.

INTRODUCTION

Until now, 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) [1]. Based on minor variations of the GAS-process, different techniques, including Aerosol Supercritical Extraction System (ASES), Precipitation with a Compressed Anti-solvent (PCA), Supercritical Anti-Solvent (SAS) and Solution Enhanced-Dispersion by Supercritical fluids (SEDS), are now in use. To verify the feasibility of these processes, the knowledge of phase behaviour of the mixtures at the process conditions is essential. With regard to the PGSS-process, the ability of the supercritical solvent to melt the solid and to form saturated liquid phase is of major interest. In case of the RESS-process the solubility of the low volatile organic substance in the supercritical fluid is one of the key properties. Moreover, the solid-liquid-gas three-phase-line (SLG-line) of the systems 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 strongly influenced by the phase behaviour of the systems involved [2,3]. However, since reliable measurements of the phase behaviour of low volatile substances and supercritical fluids are time consuming and the cost of these measurements are quite high there is a need for reducing the experimental work by applying suitable equations of state. Thus, the primary object of our investigations 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.

EQUATIONS OF STATE

For the description of the experimental results of the SLG-data various cubic equations of state where 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 [4,5]. 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 $a(T) = a_C \, \acute{} a(T)$ is treated as a function of temperature. The temperature dependence of the attraction parameter $a(T)$ was represented using the equations proposed by the authors in the respective original publications. The cubic equations of state represented by Eq. (1) where applied to the binary systems using the classical van der Waals mixing and combination rules:

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

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

$$c = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \cdot c_{ij} \qquad \text{with} \quad c_{ij} = c_{ji} = \frac{c_i + c_j}{2} \cdot \left(1 - m_{ij}\right) \tag{2c}$$

$$d = \sum_{i=1}^{n} x_i d_i \tag{2d}$$

The SLG-line can be calculated by solving Eq. (3) - (5) simultaneously, where f is the fugacity calculated from the cubic equations of state. In case that the solid-gas equilibrium (S$_2$=G) has to be calculated, Eq. (5) has to be solved only. Due to the fact, that the solid state of a pure substance cannot be represented by an conventional equation of state, it is assumed that the fugacity of the pure solid can be related to that of a so-called sub-cooled liquid reference state at a given pressure and temperature [1,6]. In Eq. (6), where Dh_i^{fus} is the enthalpy and T_i^{fus} the temperature of fusion at the triple point of the pure substance, the second term of the right hand side considers the pressure dependence. Of course, this expression neglects minor terms, which are a function of differences in heat capacities [1,6].

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

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

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

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

MODELLING RESULTS

As the SLG-line depends strongly on the solubility of the supercritical solvent in the melt of the organic solute, both the melting point depressions and the location of the UCEP can be manipulated by changing the supercritical solvent or by using supercritical solvent mixtures. Among others, the following binary systems have been investigated: CO_2/naphthalene, ethylene/naphthalene, ethane/naphthalene, CO_2/biphenyl, ethylene/biphenyl, ethane/biphenyl [2,3,7-16]. For these systems, both experimental data for the temperature and the pressure at the UCEP as well as melting points under high pressures are available in the literature. In the present investigation, the binary interaction parameters for the mixing rules applied have been fitted only to the location of the UCEP. In all calculations reported below the properties of pure solutes were taken from Schmitt and Reid [17]. For the solutes investigated, the physico-chemical properties are listed in Table 1 and the critical properties, the acentric factor and the constants A and B for calculating the vapour pressure are given in Table 2. The values of the interaction parameters regressed from UCEP are listed in Table 3 for the systems investigated. It is shown in Figure 1, that both the RKS-EoS and the PR-EoS are able to describe the naphthalene melting points in the presence of CO_2 and of ethylene acceptably well and that the position of the UCEP is accurately predicted. However, for both systems investigated the RKS-EoS yields to a slightly better description of the SLG-line than the PR-EoS. Similar results were also obtained for the systems ethane/naphthalene, and ethane/biphenyl [18]. Figure 2 compares the prediction of the RKS- and the PR-EoS with experimental melting point data for the systems CO_2/biphenyl and ethylene/biphenyl. For the later system and for both EoS an adequate agreement between experimental and calculated biphenyl melting points is noticed if the binary interaction parameters k_{12} and l_{12} were fitted to the location of the UCEP. In contrast to these results, markedly greater differences in the prediction of the SLG-line occur for the system CO_2/biphenyl. While the calculations performed with the PR-EoS lead to an insufficient description of the SLG-line, a very good agreement between experimental and calculated biphenyl melting points is noticed for the RKS-EoS. In literature, several composition data are available along the SLG-line for the system CO_2/naphthalene and CO_2/biphenyl [8,11]. In addition, both EoS are able to predict the composition of liquid and vapour phases along the SLG-line qualitatively correct [18].

CONCLUSIONS

Experimental melting points are represented by the RKS- and the PR-EoS using two binary interaction parameters fitted exclusively to the UCEP. From an engineering point of view, these EoS are able to predict the solid - fluid-, the vapor - liquid-, and the solid – liquid – gas - equilibrium of supercritical mixtures reasonably well.

Table 1: Physico-chemical properties of the solutes investigated.

Substance	T_m (K)	Δh_i^{fus} (KJ/mol)	v_i^S (cm^3/mol)	M (g/mol)
Naphthalene	353.35	19.06	128.6	128.174
Biphenyl	344.15	18.80	131.0	154.174

Table 2: Critical properties, acentric factor and vapour pressure of solutes.

Substance	T_C (K)	p_C (MPa)	ω (-)	A[1]	B[1]
Naphthalene	748.4	4.05	0.305	13.583	3733.9
Biphenyl	769.15	3.39	0.416	14.804	4367.4

Table 3: Root-Mean-Square Deviation, *RMSD*[2], between experimental and calculated melting points and values of the binary interaction parameters regressed from UCEP, N = number of experimental p - T - data.

System	EoS	N	*RMSD*	k_{ij}	l_{ij}
Carbon dioxide / Naphthalene	RKS	131	1.5×10^{-2}	0.080972	-0.036431
	PR		2.5×10^{-2}	0.074388	-0.057526
Carbon dioxide / biphenyl	RKS	46	6.3×10^{-3}	0.081477	-0.0108225
	PR		1.9×10^{-2}	0.074021	-0.040882
Ethylene / Naphthalene	RKS	50	1.5×10^{-2}	-0.004211	-0.028078
	PR		1.6×10^{-2}	0.005454	-0.038170
Ethylene / Biphenyl	RKS	33	1.4×10^{-2}	-0.012661	-0.015742
	PR		1.8×10^{-2}	-0.001413	-0.026865
Ethane / Naphthalene	RKS	17	1.5×10^{-2}	-0.009875	-0.064221
	PR		1.2×10^{-2}	0.009479	-0.073672
Ethane / Biphenyl	RKS	14	1.2×10^{-2}	-0.009979	-0.041704
	PR		1.5×10^{-2}	-0.009719	-0.059675

1) $log\ p(\ Pa\ ) = A - \dfrac{B}{T}$

2) $RMSD = \sqrt{\dfrac{1}{N}\Sigma\left(\dfrac{T_{exp} - T_{calc}}{T_{exp}}\right)^2}$
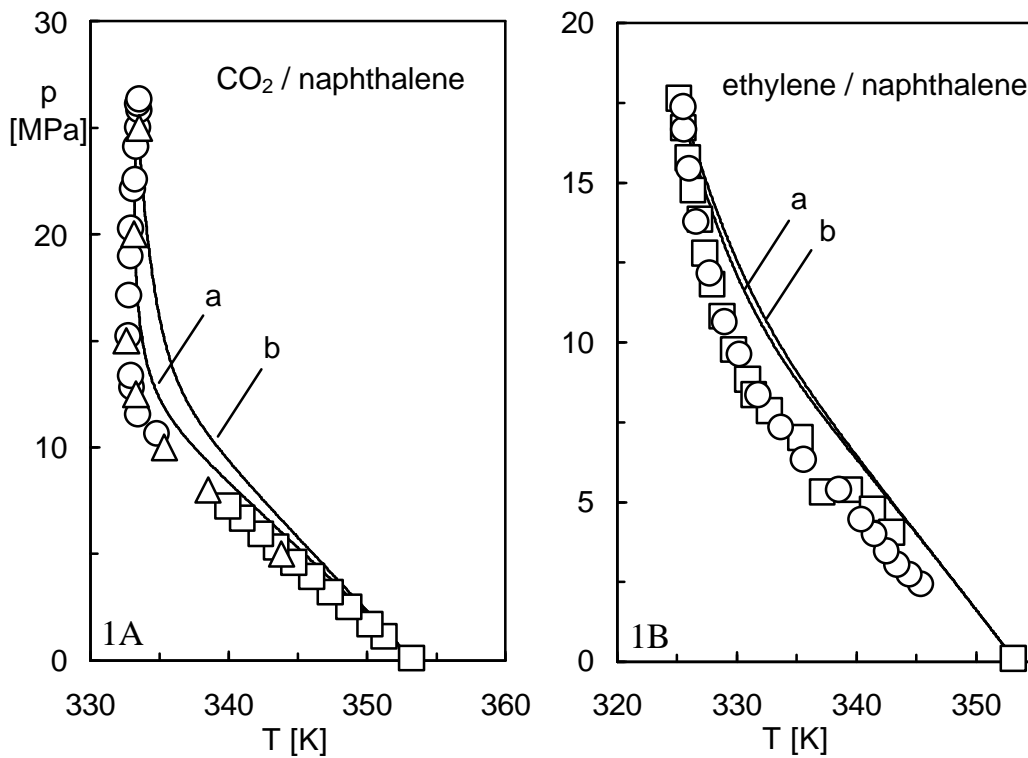
Fig. 1: Naphthalene melting points in the presence of CO$_2$ and of ethylene under high pressures, a) RKS-EoS, b) PR-EoS, Fig. 1A: ○ [2,3], □ [8], △ [12], Fig. 1B: ○ [13], □ [14].
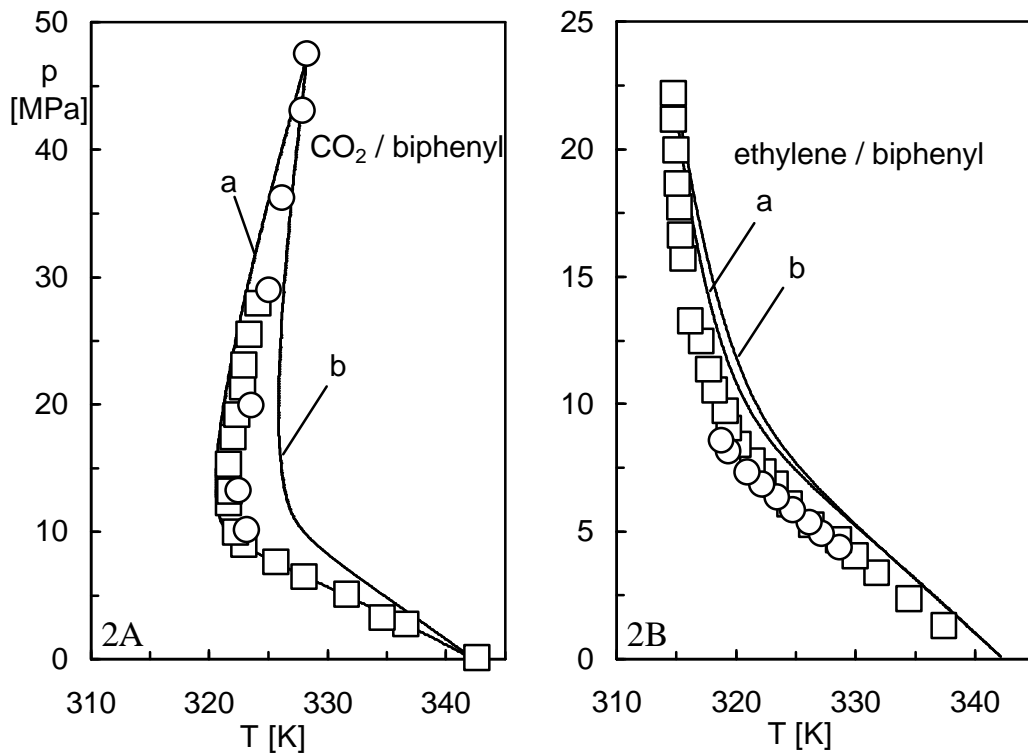

Fig. 2: Biphenyl melting points in the presence of CO$_2$ and of ethylene under high pressures, a) RKS-EoS, b) PR-EoS, Fig. 2A: ○ [7], □ [15], Fig. 2B: ○ [16], □ [13].

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