



Thermochemistry of halogenobenzoic acids as an access to PC-SAFT solubility modeling



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ABSTRACT

Absolute vapor pressures and molar sublimation enthalpies of 2-, 3-, and 4-monohalogenobenzoic acids (halogen = fluorine and iodine) were derived from transpiration measurements. Molar enthalpies of fusion were measured by DSC. Thermochemical data available in the literature were collected, evaluated, and combined with own experimental results in order to recommend sets of sublimation and fusion enthalpies. Further, the recommended data were used to estimate PC-SAFT pure-component parameters. These parameters were applied to predict the solubility of the monohalogenobenzoic acids in water at 298.15 K, yielding satisfying prediction results. This approach proved the capability of PC-SAFT to predict solid–liquid phase equilibria if precise data on sublimation pressures and fusion properties is available.

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1. Introduction

Halogenobenzoic acids are known to be toxic to biological environments, and these substances are slowly biodegraded [1]. However, several organisms are able to metabolize (oxidize, dehalogenate, mineralize) monohalogenobenzoates [2–5], meaning that these organisms can grow using halogenobenzoic acids as carbon source. Comparative metabolism of different halogenobenzoic acids is thus important for general understanding of metabolic pathways involving halogenobenzoic acids [6]. The reliability of modeling metabolic processes depends on the quality of experimental thermochemical input data. Such data include formation properties such as Gibbs energy of formation, which data are accessible by combination of vapor pressure measurements with calorimetric studies [7]. In recent works, these

thermochemical properties were evaluated for chlorobenzoic acids and bromobenzoic acids [8,9]. Available experimental data on fluoroobenzoic acids and iodobenzoic acids already exist, but are still scarce [10–16]. Thus, additional experimental studies are desired that allow recommending a precise set of data. Mutually consistent results can be obtained by independently measured data (using different techniques), which can then be used as a basis for analysis and evaluation of available data.

Aqueous solubility of biomolecules and chemicals is an important property that is required for crystallization processes. Further, aqueous solubility has to be known for analyzing metabolic processes as solubility presents the maximum amount of a compound that is present in a liquid aqueous environment. Benzoic acid derivatives are known to be sparingly soluble in water. Data on aqueous solubility are scarcely available in the literature [17], and often given at room temperature only. Thus, a thermodynamic model is desired which is able to predict solubility. State-of-the-art g^E models (e.g. NRTL, UNIQUAC) require typically 3–5 binary parameters in order to calculate phase equilibria such as solubility in water. The drawback of such g^E -models is that they do not allow solubility predictions as binary parameters are required. Even

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worse, mathematics forbids fitting 3–5 parameters to only one experimental data point, i.e. solubility in water at room temperature. The use of equations of state might solve these drawbacks. Usually, pure-component parameters are used to describe a mixture, and often one binary parameter is fitted to phase-equilibrium data. Thus, equations of state allow either correlating solubility (by fitting the binary parameter to room temperature solubility in water) or even predicting solubility (by setting the binary parameter to zero).

Quantitatively predicting water solubility of biological components using equations of state is still a challenging task. Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [18] seems to be a promising tool for this purpose. Previous works have shown that PC-SAFT allows quantitatively correlating solubility of amino acids [19–21] and osmolytes or urea [22–24]. PC-SAFT has also been used to predict solubility of sugars and amino acids [25,26]. However, in all these works pure-component parameters were estimated based on data of binary aqueous solutions such as mixture densities or osmotic coefficients. Such data is not available for the monohalogenobenzoic acids considered in this work, caused by the very poor solubility of these components in water.

A recent study has shown that it was possible to estimate pure-component parameters for the biomolecules adenine and cytosine based on experimental vapor pressures of the pure compounds [27]. Thus, joint treatment of consistent own and literature results for each compound under study helps to avoid a possible systematic error in order to recommend evaluated data sets for use in further thermochemical calculations, metabolic models, and parametrization of equations of state.

In this work, vapor pressure measurements on 2-, 3-, and 4-isomers of fluorobenzoic acid and iodobenzoic acid as well as their fusion properties were measured. Pure-component parameters required for PC-SAFT solubility calculations were obtained from these experimental data. This work is a continuation of our previous research on modeling and predicting phase equilibria of benzoic acid and chlorobenzoic acid [Held 2015].

2. Materials and methods

2.1. Materials

Samples of the monohalogenobenzoic acids were of commercial origin with purities between 97w% and 99w%. Samples were further purified by fractional sublimation in vacuum. No impurities (greater than 0.001 mass fractions) were detected in samples used for the vapor pressure measurements analyzed using GC and DSC techniques. Provenance and purity of samples studied in this work are given in Table 1.

2.2. Transpiration method. Vapor pressure measurements

Vapor pressures of the monohalogenobenzoic acids were measured using the transpiration method, which is described in detail in Refs. [28,29]. About 0.5 g of a solid sample was dissolved in

acetonitrile and mixed with small glass beads in a glass beaker. Under vigorous stirring with a spatula and gentle heating the solvent was removed from the beaker producing glass beads covered uniformly with the sample. These covered glass beads were placed in a thermostatted U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample was determined by weighing with microbalances of 0.0001 g resolution. The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with substance i , values of p_i were calculated with Eq. (1):

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i; \quad V = V_{N_2} + V_i; \quad (V_{N_2} \gg V_i) \quad (1)$$

where $R = 8.314462 \text{ J K}^{-1} \text{ mol}^{-1}$; m_i is the mass of the transported compound i , M_i is the molar mass of the compound i , and V_i its volume contribution to the gaseous phase. V_{N_2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N_2} was determined from the flow rate and the time measurement. Uncertainties of absolute vapor pressures measured by the transpiration method were estimated according to the procedure described in detail in Ref. [29].

2.3. DSC. Enthalpy of fusion measurements

The thermal behavior of monohalogenobenzoic acids including fusion temperature and enthalpies of fusion was studied with a Mettler Toledo 822 in hermetically closed pans with a heating rate of 10 K min^{-1} . The calorimeter was calibrated using the reference material indium having purity of a mass fraction of 0.9999. The DSC measurements were repeated in triplicate and values agreed within the experimental uncertainties $u(\Delta h^{SL}) = 0.2 \text{ kJ mol}^{-1}$ for the enthalpy of fusion and $u(T^{SL}) = 0.5 \text{ K}$ for the fusion temperature assigned as a peak ongoing temperature.

2.4. PC-SAFT

In order to model the pure-fluid behavior of monohalogenobenzoic acids as well as the solubility of monohalogenobenzoic acids in water, original PC-SAFT [18] was applied in this work. The residual Helmholtz energy a^{res} that serves as a basis for all calculations within the PC-SAFT framework was expressed as the sum of single Helmholtz energies a^{hc} due to hard-chain repulsion, a^{disp} for dispersion interactions, and a^{assoc} accounting for hydrogen bonding forces.

$$a^{res} = a^{hc} + a^{disp} + a^{assoc} \quad (2)$$

Eq. (2) presents the expression of original PC-SAFT by Gross and Sadowski [18], and neither multi-polar nor ionic interactions were considered in this work.

The monohalogenobenzoic acids and water were modeled as

Table 1
Sample provenance table and purity of the components after purification. SA = Sigma–Aldrich Co. LLC.

Compound, IUPAC name	CAS number	Supplier	Purification method	DSC purity (mass fraction)
2-fluorobenzoic acid	445-29-4	SA, 97%	fractional sublimation	0.999
3-fluorobenzoic acid	455-38-9	SA, 97%	fractional sublimation	0.999
4-fluorobenzoic acid	456-22-4	SA, 99%	fractional sublimation	0.999
2-iodobenzoic acid	88-67-5	SA, 98%	fractional sublimation	0.999
3-iodobenzoic acid	618-51-9	SA, 98%	fractional sublimation	0.999
4-iodobenzoic acid	619-58-9	SA, 98%	fractional sublimation	0.998

associating fluids assigned with two association sites each, mimicking one proton donor and one proton acceptor, respectively. This is commonly known as the 2B association approach according to Huang and Radosz [30]. Thus, in sum five pure-component parameters are required to characterize one compound i with PC-SAFT, segment diameter σ_i , segment number m_i^{seg} , dispersion-energy parameter u_i/k_B , association-energy parameter ϵ^{AiBi}/k_B and association-volume parameter κ^{AiBi} . Combining rules were applied to describe mixtures based on these pure-component PC-SAFT parameters. According to our previous work [Held 2015], the standard combining rules of Lorentz and Berthelot were used for the segment diameter σ_{ij} and for the dispersion-energy parameter u_{ij} . In order to describe the associative behavior of mixtures, Wolbach and Sandler rules were used that are based on the pure-component association parameters of the components i and j .

Application of Eq. (2) for the description of a system combined with the combining rules allow for modeling phase equilibria. In this work, solid-vapor phase equilibrium of pure monohalogenobenzoic acids as well as solid–liquid phase equilibrium of binary mixtures water/monohalogenobenzoic acids were modeled with PC-SAFT. In order to calculate vapor pressures of the solid monohalogenobenzoic acids, the isofugacity criterion was applied according to [27]. In order to model solubilities with PC-SAFT, a simplified solid–liquid equilibrium condition was applied that neglects heat-capacity effects, as the latter have only a marginal influence for the mixtures and the temperature range considered in this work:

$$x_i^L = \frac{\varphi_{0i}}{\varphi_i} \cdot \exp\left\{\frac{\Delta h_{0i}^{SL}}{RT} \left(1 - \frac{T_{0i}^{SL}}{T}\right)\right\} \quad (3)$$

Application of Eq. (3) requires the fusion properties of the monohalogenobenzoic acid i , i.e. the fusion enthalpy Δh^{SL} and the fusion temperature T^{SL} , respectively. The fugacity coefficients of the monohalogenobenzoic acids i in the pure-compound state (φ_{0i}) and in the mixture with water at saturated conditions (φ_i) were modeled with PC-SAFT. The expression for the fugacity coefficients can be found elsewhere, e.g. Ref. [27].

3. Results and discussion

3.1. Vapor pressures of the fluorobenzoic acids and iodobenzoic acids

Absolute vapor pressures p_i measured by the transpiration method were fitted using the following equation:

$$\ln(p_i/p^0) = \frac{a}{R} + \frac{b}{RT} + \frac{\Delta_{cr}^g C_{p,m}^0}{R} \cdot \ln\left(\frac{T}{T_0}\right) \quad (4)$$

where a and b are adjustable parameters and $\Delta_{cr}^g C_{p,m}^0$ is the difference of the molar heat capacities of the gaseous and the crystalline phase respectively. T_0 appearing in Eq. (4) is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K) and R is the molar gas constant. In order to fit the two parameters a and b , values of $\Delta_{cr}^g C_{p,m}^0$ were required. These were calculated according to the procedure developed by Chickos and Acree [31] based on the isobaric molar heat capacities $C_{p,m}^0(\text{cr}, 298.15 \text{ K})$. The latter values were estimated by group-additivity [32]. The resulting values of $\Delta_{cr}^g C_{p,m}^0$ were $-25.5 \text{ J K}^{-1} \text{ mol}^{-1}$ for the fluorobenzoic acids and $-25.9 \text{ J K}^{-1} \text{ mol}^{-1}$ for the iodobenzoic acids, as listed in Table S1 in the supporting material. The results of our vapor pressure measurements of fluorobenzoic acids are listed in Table 2, and the results of our vapor pressure measurements of iodobenzoic acids are summarized in Table 3. This includes the (p_i, T) data as well

as the coefficients a and b , respectively.

Vapor pressures of fluorobenzoic acids and iodobenzoic acids that were available from literature [10,11] were compared to the absolute vapor pressures measured in this work, and the results are graphically illustrated in Figs. S1–S6 of the supplementary material. Our new data measured with the transpiration method are in good agreement with results from the Knudsen effusion method [10]; however, a direct comparison of both data sets is not possible due to different temperature regions considered in our work and in the work of Monte et al. [10]. At the same time, vapor pressures for 4-fluorobenzoic acid measured in this work are in close agreement with results reported by Cox et al. [11] also from the transpiration method.

3.2. Sublimation enthalpies of monohalogenobenzoic acids

Sublimation enthalpy was calculated from equation:

$$\Delta_{cr}^g H_m^0(T) = -b + \Delta_{cr}^g C_{p,m}^0 \cdot T \quad (5)$$

Values of $\Delta_{cr}^g C_{p,m}^0$ were used according to Table S1 in the supporting material, as already applied in Eq. (4). Sublimation entropies at temperature T were also derived from the temperature dependence of vapor pressure data using Eq. (6):

$$\Delta_{cr}^g S_m^0(T) = \Delta_{cr}^g H_m^0(T)/T + R \ln(p_i/p^0) \quad (6)$$

The values of $\Delta_{cr}^g H_m^0(T)$ and $\Delta_{cr}^g S_m^0(T)$ are given in Tables 2 and 3. Procedure for calculation of the combined uncertainties of the sublimation enthalpy was described elsewhere [29]. The combined uncertainties include uncertainties of the experimental conditions of the transpiration method, uncertainties of vapor pressure, and uncertainties of temperature adjustment to 298.15 K.

Sublimation enthalpies $\Delta_{cr}^g H_m^0(298.15 \text{ K})$ of the benzoic acid derivatives published in literature [10–16] were adjusted to the reference temperature 298.15 K in a different way and with the different $\Delta_{cr}^g C_{p,m}^0$ -values compared to our data reduction method. We treated the literature vapor pressures uniformly using Eqs. (4) and (5) and calculated $\Delta_{cr}^g H_m^0(298.15 \text{ K})$ for the sake of comparison with our results (see Table 4).

Sublimation enthalpies $\Delta_{cr}^g H_m^0(298.15 \text{ K})$ for fluorobenzoic acids from this work and from literature are collected in Table 4. Our new results are in agreement with the result from the Knudsen-effusion method [10] and from the transpiration method within experimental uncertainty. Sublimation enthalpies $\Delta_{cr}^g H_m^0(298.15 \text{ K})$ for iodobenzoic acids from this work and from literature are summarized in Table 4. In contrast to the fluorobenzoic acids, available experimental data for iodobenzoic acids are less consistent. Our new results for all three isomers are in agreement (within experimental uncertainty) with the result from the Knudsen-effusion method [10] but in significant disagreement with the direct calorimetric results reported Tan and Sabbah [13]. From our experiences, the sublimation enthalpies measured by R. Sabbah with the Tian-Calvet flux-calorimeter equipped with the Knudsen cell [13] are often in disagreement with other available data; inconsistencies have already been observed for 4-chlorobenzoic acid [8] and bromobenzoic acids [9].

In order to establish more confidence in $\Delta_{cr}^g H_m^0(298.15 \text{ K})$ -values for fluorobenzoic acids and iodobenzoic acids, the mean average value for each compound using the uncertainty of sublimation enthalpy as weighing factor were calculated. These values are listed in Table 4 and are recommended for further thermochemical calculations.

Table 2
Absolute vapor pressures p , sublimation enthalpies, $\Delta_{cr}^{\circ}H_m^{\circ}$, and sublimation entropies, $\Delta_{cr}^{\circ}S_m^{\circ}$, of fluorobenzoic acids obtained by the transpiration method.

T/K^a	m/mg^b	$V(N_2)^c/dm^3$	T_a/K^d	Flow/ $dm^3 \cdot h^{-1}$	p/Pa^e	$u(p)/Pa^f$	$\Delta_{cr}^{\circ}H_m^{\circ}/kJ \cdot mol^{-1}$	$\Delta_{cr}^{\circ}S_m^{\circ}/J \cdot K^{-1} \cdot mol^{-1}$
2-fluorobenzoic acid; $\Delta_{cr}^{\circ}H_m^{\circ}(298.15 \text{ K}) = (96.1 \pm 0.8) \text{ kJ mol}^{-1}$								
$\ln(p/p^{\circ}) = \frac{323.11}{K} - \frac{103661.01}{K \cdot (T/K)} - \frac{25.5}{K} \ln\left(\frac{T/K}{298.15}\right)$								
333.9	9.3	51.80	296.2	4.20	3.21	0.09	95.15	199.0
334.6	11.0	56.03	296.2	3.48	3.50	0.09	95.13	199.1
335.9	10.3	46.89	294.2	4.44	3.89	0.10	95.10	198.7
337.0	14.2	56.03	296.2	3.48	4.51	0.12	95.07	198.9
338.9	14.4	48.41	296.2	3.64	5.28	0.14	95.02	198.5
340.2	11.1	32.04	296.2	5.36	6.14	0.18	94.99	198.6
342.0	10.6	25.59	298.2	3.57	7.38	0.21	94.94	198.5
342.2	9.7	23.59	298.5	4.26	7.34	0.21	94.94	198.3
345.0	9.9	18.72	298.0	4.32	9.40	0.26	94.86	197.9
346.6	10.1	16.00	296.2	3.49	11.15	0.30	94.82	197.9
348.3	11.0	14.71	296.2	4.20	13.20	0.35	94.78	197.9
351.2	10.1	10.42	296.2	4.22	17.09	0.45	94.71	197.6
352.4	5.8	5.119	296.2	4.95	19.97	0.52	94.68	197.9
353.2	9.7	8.190	296.2	3.64	20.87	0.55	94.66	197.6
354.2	10.4	8.171	296.2	4.26	22.42	0.59	94.63	197.3
356.5	9.3	5.684	298.5	4.26	29.03	0.75	94.57	197.6
358.2	11.7	6.060	296.2	3.60	33.98	0.87	94.53	197.5
358.3	10.2	5.611	298.0	4.21	32.20	0.83	94.53	197.0
360.5	10.2	4.521	298.2	4.31	39.97	1.02	94.47	197.0
361.3	9.8	3.890	295.9	3.48	44.28	1.13	94.45	197.2
363.4	10.2	3.564	294.2	4.36	50.01	1.28	94.40	196.6
364.5	9.5	3.019	295.9	3.48	55.29	1.41	94.37	196.6
367.2	10.0	2.439	295.9	3.48	72.04	1.83	94.30	196.7
3-fluorobenzoic acid; $\Delta_{cr}^{\circ}H_m^{\circ}(298.15 \text{ K}) = (93.3 \pm 0.9) \text{ kJ mol}^{-1}$								
$\ln(p/p^{\circ}) = \frac{318.47}{K} - \frac{100878.40}{K \cdot (T/K)} - \frac{25.5}{K} \ln\left(\frac{T/K}{298.15}\right)$								
331.9	10.5	46.16	296.2	3.48	4.07	0.11	92.42	194.4
334.9	17.4	54.91	296.2	3.33	5.64	0.15	92.34	194.4
338.0	15.3	37.03	296.2	3.36	7.34	0.21	92.26	193.8
342.1	10.3	15.99	296.2	3.69	11.39	0.31	92.16	193.9
345.0	12.0	14.40	296.2	3.60	14.72	0.39	92.08	193.6
347.1	9.8	9.697	296.2	3.48	17.83	0.47	92.03	193.4
350.4	9.9	7.417	296.2	3.56	23.53	0.61	91.94	193.0
353.3	9.9	5.642	296.2	3.64	30.91	0.80	91.87	192.9
356.5	10.0	4.274	296.2	3.29	41.19	1.05	91.79	192.7
359.5	10.2	3.306	296.2	3.31	54.30	1.38	91.71	192.6
362.6	9.8	2.519	296.2	3.44	68.45	1.74	91.63	192.2
4-fluorobenzoic acid; $\Delta_{cr}^{\circ}H_m^{\circ}(298.15 \text{ K}) = (93.9 \pm 0.7) \text{ kJ mol}^{-1}$								
$\ln(p/p^{\circ}) = \frac{312.04}{K} - \frac{101450.89}{K \cdot (T/K)} - \frac{25.5}{K} \ln\left(\frac{T/K}{298.15}\right)$								
343.0	12.2	47.27	296.2	3.22	4.56	0.12	92.71	187.2
346.2	12.9	37.22	296.2	3.15	6.12	0.18	92.62	186.9
349.3	14.2	29.66	296.2	2.25	8.44	0.24	92.55	187.0
355.1	9.7	12.34	296.2	3.09	13.84	0.37	92.40	186.4
356.5	10.9	12.47	296.2	3.22	15.39	0.41	92.36	186.1
359.5	11.0	9.231	296.2	3.18	20.97	0.55	92.28	186.3
363.7	9.8	6.026	296.2	3.29	28.61	0.74	92.18	185.6
365.6	6.2	3.169	296.2	3.17	34.41	0.89	92.13	185.7
366.9	12.5	5.896	296.2	3.31	37.29	0.96	92.10	185.4
371.8	10.0	3.184	296.2	3.41	55.23	1.41	91.97	185.0
375.8	9.9	2.264	296.2	3.40	76.88	1.95	91.87	184.9
380.9	10.9	1.649	296.2	3.41	116.22	2.93	91.74	184.7
385.2	9.6	1.052	294.2	3.32	159.37	4.01	91.63	184.3
386.2	7.5	0.775	296.2	3.10	170.10	4.28	91.60	184.2

^a Saturation temperature with $u(T) = 0.1 \text{ K}$.

^b Mass of transferred sample condensed at $T = 273 \text{ K}$.

^c Volume of nitrogen ($u(V) = 0.005 \text{ dm}^3$) used to transfer m ($u(m) = 0.0001 \text{ g}$) of the sample.

^d T_a is the temperature of the soap bubble meter used for measurement of the gas flow.

^e Vapor pressure at temperature T calculated from the m and the residual vapor pressure at $T = 273 \text{ K}$ calculated by an iteration.

^f Uncertainties were calculated with $u(p/Pa) = 0.005 + 0.025(p/Pa)$ for pressures below 5 Pa and with $u(p/Pa) = 0.025 + 0.025(p/Pa)$ above 5 Pa.

3.3. Enthalpies of fusion of halogen benzoic acids

Fusion temperatures and enthalpies of fusion of the monohalogenobenzoic acids measured in the present work and those available from the literature are compiled in Table 5. Phase transitions other than melting or fusion of samples under study have not

been detected. Experimental enthalpies of fusion measured by DSC (see Table 4) were obtained at the fusion temperature T^{SL} . Because T^{SL} did not present the reference temperature in this work, the experimental enthalpies of fusion were adjusted to $T = 298.15 \text{ K}$ by Eq. (7) [31]:

Table 3Absolute vapor pressures p , sublimation enthalpies, $\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$, and sublimation entropies, $\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}$, of iodobenzoic acids obtained by the transpiration method.

T/K^{a}	m/mg^{b}	$V(\text{N}_2)^{\text{c}}/\text{dm}^3$	$T_{\text{a}}/\text{K}^{\text{d}}$	$\text{Flow}/\text{dm}^3 \cdot \text{h}^{-1}$	p/Pa^{e}	$u(p)/\text{Pa}^{\text{f}}$	$\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}/\text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$
2-iodobenzoic acid; $\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}(298.15 \text{ K}) = (111.4 \pm 0.8) \text{ kJ mol}^{-1}$								
$\ln(p/p^{\circ}) = \frac{334.9}{R} - \frac{119166.47}{R \cdot (T/\text{K})} - \frac{25.9}{R} \ln\left(\frac{T/\text{K}}{298.15}\right)$								
362.4	7.2	63.21	296.2	4.78	1.13	0.03	109.78	208.3
367.6	10.8	57.40	298.2	4.65	1.88	0.05	109.65	207.8
376.2	9.7	22.16	294.2	4.72	4.32	0.11	109.42	207.3
381.9	11.0	14.77	298.0	4.92	7.44	0.21	109.28	207.1
386.9	10.1	9.178	298.0	5.01	10.99	0.30	109.15	206.4
393.2	8.4	4.162	296.2	4.54	20.04	0.53	108.98	206.4
393.2	11.4	6.084	298.5	5.14	18.75	0.49	108.98	205.9
397.2	4.0	1.438	295.9	4.79	27.59	0.71	108.88	206.0
399.2	10.9	3.415	298.5	5.12	31.93	0.82	108.83	205.7
403.2	10.8	2.387	296.2	4.77	44.92	1.15	108.72	205.6
403.2	10.5	2.402	294.2	5.34	43.10	1.10	108.72	205.3
407.3	10.1	1.650	296.2	4.95	60.78	1.54	108.62	205.1
411.5	11.0	1.250	296.2	5.00	87.37	2.21	108.51	205.2
3-iodobenzoic acid; $\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}(298.15 \text{ K}) = (109.1 \pm 0.8) \text{ kJ mol}^{-1}$								
$\ln(p/p^{\circ}) = \frac{325.42}{R} - \frac{116779.15}{R \cdot (T/\text{K})} - \frac{25.9}{R} \ln\left(\frac{T/\text{K}}{298.15}\right)$								
366.6	11.3	92.94	297.5	5.31	1.21	0.04	107.29	198.6
370.4	15.0	87.25	297.5	5.45	1.71	0.05	107.19	198.2
375.8	10.6	37.63	297.5	8.36	2.81	0.08	107.05	197.8
380.8	10.3	23.44	297.5	8.27	4.38	0.11	106.92	197.4
386.0	12.1	17.55	297.5	5.40	6.88	0.20	106.78	197.0
389.1	11.2	12.49	297.5	5.17	8.94	0.25	106.70	196.8
391.9	10.6	9.000	297.5	5.14	11.74	0.32	106.63	196.9
395.1	10.8	7.081	297.5	5.31	15.21	0.41	106.55	196.6
399.2	10.5	5.063	297.5	5.06	20.68	0.54	106.44	196.1
404.1	17.2	5.450	297.4	5.45	31.46	0.81	106.31	196.1
404.2	19.2	6.086	297.4	5.45	31.45	0.81	106.31	196.0
409.0	12.9	2.746	297.5	5.49	46.84	1.20	106.19	195.9
411.4	21.3	3.977	297.4	4.77	53.39	1.36	106.13	195.3
414.2	10.0	1.543	297.4	5.14	64.61	1.64	106.05	195.0
417.5	10.9	1.286	297.4	5.14	84.51	2.14	105.97	195.0
422.0	18.1	1.511	297.4	4.77	119.4	3.01	105.85	194.9
4-iodobenzoic acid; $\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}(298.15 \text{ K}) = (111.2 \pm 1.0) \text{ kJ mol}^{-1}$								
$\ln(p/p^{\circ}) = \frac{318.48}{R} - \frac{118895.07}{R \cdot (T/\text{K})} - \frac{25.9}{R} \ln\left(\frac{T/\text{K}}{298.15}\right)$								
388.9	14.5	70.89	298.3	5.89	2.05	0.06	108.82	190.1
391.1	13.2	54.19	298.3	5.03	2.44	0.07	108.77	189.8
403.3	9.9	15.14	298.3	5.34	6.54	0.19	108.45	188.8
409.4	10.0	9.247	298.3	5.55	10.81	0.30	108.29	188.6
415.3	9.9	5.679	298.3	5.24	17.43	0.46	108.14	188.5
421.5	10.2	3.815	298.3	5.45	26.73	0.69	107.98	187.8
424.5	11.9	3.487	298.4	5.98	34.13	0.88	107.90	187.8
427.4	11.7	2.842	298.4	5.68	41.18	1.05	107.83	187.5
433.5	9.4	1.490	298.4	5.59	63.12	1.60	107.67	187.1

^a Saturation temperature with $u(T) = 0.1 \text{ K}$.^b Mass of transferred sample condensed at $T = 273 \text{ K}$.^c Volume of nitrogen ($u(V) = 0.005 \text{ dm}^3$) used to transfer m ($u(m) = 0.0001 \text{ g}$) of the sample.^d T_{a} is the temperature of the soap bubble meter used for measurement of the gas flow.^e Vapor pressure at temperature T calculated from the m and the residual vapor pressure at $T = 273 \text{ K}$ calculated by an iteration.^f Uncertainties were calculated with $u(p/\text{Pa}) = 0.005 + 0.025(p/\text{Pa})$ for pressures below 5 Pa and with $u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa})$ above 5 Pa.

$$\begin{aligned} & \left\{ \Delta h^{\text{SL}}(T^{\text{SL}}/\text{K}) - \Delta h^{\text{SL}}(298 \text{ K}) \right\} / (\text{J} \cdot \text{mol}^{-1}) \\ & = \left\{ (0.75 + 0.15C_{p,m}^{\circ, \text{cr}}) \left[(T^{\text{SL}}/\text{K}) - 298 \text{ K} \right] \right\} - \left\{ (10.58 \right. \\ & \quad \left. + 0.26C_{p,m}^{\circ, \text{liq}}) \left[(T^{\text{SL}}/\text{K}) - 298 \text{ K} \right] \right\} \end{aligned} \quad (7)$$

where $C_{p,m}^{\circ, \text{cr}}$ and $C_{p,m}^{\circ, \text{liq}}$ are the isobaric molar heat capacities of the solid and the liquid halogenobenzoic acids (given in Table S1 in the supporting material). With these adjustments molar enthalpies of fusion, $\Delta h^{\text{SL}}(298.15 \text{ K})$, were calculated (see Table 5). Uncertainties in the temperature adjustment of fusion enthalpies from T^{SL} to the reference temperature are estimated to account with <30% to the total adjustment [33].

Data sets on fusion enthalpies of both, fluorobenzoic acids and iodobenzoic acids are consistent for each isomer. In order to establish more confidence in $\Delta h^{\text{SL}}(298.15 \text{ K})$ -values for fluorobenzoic acids and iodobenzoic acids, the mean average value for each compound was calculated using the uncertainty of fusion enthalpy as the weighing factor (see Table 5). These values are recommended for further thermochemical calculations.

3.4. PC-SAFT modeling

3.4.1. Parameter estimation

The pure-component parameters for water are available in the literature. The original parameter set for water from Fuchs et al. [34] is usually most promising for phase equilibrium modeling at temperatures below 100 °C. The temperature dependence of the

Table 4
Compilation of data on enthalpies of sublimation, $\Delta_{cr}^g H_m^o$, of fluorobenzoic acids and iodobenzoic acids.

Compound	Method ^a	T-range/K	$\Delta_{cr}^g H_m^o / T_{av}$ kJ mol ⁻¹	$\Delta_{cr}^g H_m^o / 298.15$ K ^b kJ mol ⁻¹	Ref
fluorobenzoic acids					
2-fluorobenzoic acid	ME	309.1–323.2	93.9 ± 0.5	94.4 ± 0.9	[10]
	T	333.9–367.2	94.8 ± 0.4	96.1 ± 0.8 95.3 ± 0.6^d	This work Average
3-fluorobenzoic acid	ME	303.2–317.2	93.3 ± 0.5	93.6 ± 0.9	[10]
	T	331.9–362.6	92.0 ± 0.5	93.3 ± 0.9 93.4 ± 0.6^d	This work Average
4-fluorobenzoic acid	T	358.9–381.7	91.1 ± 0.8	92.9 ± 1.1	[11]
	T	343.0–386.2	92.2 ± 0.4	93.8 ± 0.7 93.5 ± 0.6^d	This work Average
iodobenzoic acids					
2-iodobenzoic acid	DSC	440–480	76.7 ± 0.4 ^c	(88.7 ± 2.0) ^c	[12]
	C	363	90.0 ± 0.2	(91.7 ± 1.2)	[13]
	ME	345.2–359.2	111.4 ± 0.8	112.8 ± 1.1	[10]
	T	362.4–411.5	109.2 ± 0.5	111.4 ± 0.8 111.9 ± 0.7^d	This work Average
3-iodobenzoic acid	C	363	94.2 ± 0.2	(95.9 ± 1.2)	[13]
	ME	347.2–363.2	109.6 ± 0.5	111.1 ± 0.8	[10]
	T	366.6–422.0	106.6 ± 0.4	109.1 ± 0.8 110.1 ± 0.6^d	This work Average
4-iodobenzoic acid	C	363	97.7 ± 0.3	(99.4 ± 1.1)	[13]
	ME	363.2–379.1	111.0 ± 0.5	112.9 ± 0.8	[10]
	T	388.9–433.5	108.3 ± 0.5	111.2 ± 1.0 112.2 ± 0.6^d	This work Average

^a Methods: DSC = differential scanning calorimetry. ME = Knudsen effusion method; C = Tian-Calvet microcalorimeter equipped with the Knudsen cell; T = transpiration method.

^b Uncertainties of sublimation enthalpies are expressed in this Table as standard deviations. Vapor pressures available in literature were treated using Eqs. (4) and (5) in order to evaluate enthalpy of vaporization at 298.15 K in the same way as our own results.

^c Vaporisation enthalpy.

^d Average values were calculated using the uncertainty of the experiment as a weighing factor. Values in brackets were disregarded by the averaging. Recommended values are given in bold.

Table 5
Compilation of experimental data on fusion properties of fluorobenzoic acids and iodobenzoic acids.

Compounds	T^{SL}	Δh^{SL}	Δh^{SL}
	K	at T^{SL} kJ mol ⁻¹	at 298.15 K kJ mol ⁻¹
fluorobenzoic acids			
2-fluorobenzoic acid	397.4	20.1 ± 0.1 ^a [14]	15.9 ± 1.3
	396.7	20.3 ± 0.2	16.1 ± 1.3 16.0 ± 0.9^a
3-fluorobenzoic acid	395.9	18.5 ± 0.1	14.3 ± 1.3
4-fluorobenzoic acid	451	20.9 ± 0.1 [15]	14.4 ± 1.9
	456.1	21.6 ± 0.1	14.8 ± 1.9
iodobenzoic acids			
2-iodobenzoic acid	—	26.2 ± 0.2 [12]	19.6 ± 2.0
	435.1	21.4 ± 0.2 [13]	(14.8 ± 2.0)
	434.5	27.6 ± 0.1	21.0 ± 2.0 20.3 ± 1.4^a
3-iodobenzoic acid	460.4	28.7 ± 0.2 [13]	20.9 ± 2.3
	458.9	27.7 ± 0.1	20.0 ± 2.3 20.5 ± 1.6^a
4-iodobenzoic acid	543.7	35.2 ± 0.1 [13]	23.4 ± 3.5
	544.7	33.9 ± 0.8 [16]	22.1 ± 3.5
	543.9	33.7 ± 0.3	21.9 ± 3.5 22.5 ± 2.0^a

^a Average values were calculated using the uncertainty of the experiment as a weighing factor. Value in round brackets was disregarded by the averaging. Recommended values are given in bold.

segment diameter of this parameter set is of negligible importance in this work, as the modeling of the mixtures with water in the present work is related to a very narrow temperature range.

In a recent work [Held2015], PC-SAFT was applied to model phase equilibria of benzoic acid and chlorobenzoic acids. In that work, the association parameters ϵ^{AiBi}/k_B and κ^{AiBi} for the chlorobenzoic acids were inherited from benzoic acid. This procedure was adopted also in the present work, i.e. ϵ^{AiBi}/k_B was set to 1972.59 K and κ^{AiBi} was fixed to $3.06 \cdot 10^{-4}$, respectively. Vapor pressures of the pure monohalogenobenzoic acids measured in this work p_k^{exp} have been used for the estimation of the three pure-component PC-SAFT parameters (σ_i , m_i^{seg} , u_i) of iodobenzoic acids and fluorobenzoic acids by minimizing the following objective function OF:

$$OF = \sum_{k=1}^{NP} \left(\frac{p_k^{exp} - p_k^{mod}}{p_k^{exp}} \right)^2 \quad (8)$$

Further, it was paid attention to the calculation of densities of the monohalogenobenzoic acids. Each parameter set obtained with Eq. (8) was used to calculate the density of the monohalogenobenzoic acid under consideration. Only if the PC-SAFT modeled density was found to be in the range of 1300 kg/m³ for the fluorobenzoic acids and 2000 kg/m³ for the iodobenzoic acids, respectively, the parameter estimation was finished for that component. The so-obtained pure-component parameters of the monohalogenobenzoic acids are listed in Table 6.

Table 6

Pure-component PC-SAFT parameters for water and monohalogenobenzoic acids determined in this work, and binary interaction parameter between chlorobenzoic acids and water taken from literature [Held 2015].

Compound	Ref.	m_i^{seg}	$\sigma_i/\text{\AA}$	$u_i/k_B/K$	$\epsilon^{AIBi}/k_B/K$	κ^{AIBi}	T^{SL}/K	$\Delta h^{SL}/R/K$	k_{ij} with water
water ^b	[35]	1.2047	a	353.95	2425.67	0.0451	–	–	–
2-chloro benzoic acid ^b	Held 2015	8.0774	2.6075	251.70	1972.59	$3.06 \cdot 10^{-4}$	414.1	3161.95	–0.01
3-chloro benzoic acid ^b	Held 2015	8.1394	2.622	251.74	1972.59	$3.06 \cdot 10^{-4}$	427.83	2645.98	0.01
4-chloro benzoic acid ^b	Held 2015	8.5943	2.5797	259.24	1972.59	$3.06 \cdot 10^{-4}$	512.9	3968.97	0
2-iodo benzoic acid ^b	This work	11.3496	2.4717	225.76	1972.59	$3.06 \cdot 10^{-4}$	434.5	3319.50	0
3-iodo benzoic acid ^b	This work	11.2785	2.4811	229.61	1972.59	$3.06 \cdot 10^{-4}$	458.9	3331.53	0
4-iodo benzoic acid ^b	This work	12.7358	2.3831	229.61	1972.59	$3.06 \cdot 10^{-4}$	543.9	4053.16	0
2-fluoro benzoic acid ^b	This work	6.7737	2.6049	265.76	1972.59	$3.06 \cdot 10^{-4}$	396.7	2441.52	0
3-fluoro benzoic acid ^b	This work	6.9648	2.7782	257.13	1972.59	$3.06 \cdot 10^{-4}$	395.9	2225.03	0
4-fluoro benzoic acid ^b	This work	6.2185	2.9015	281.10	1972.59	$3.06 \cdot 10^{-4}$	456.1	2597.87	0

^a The expression $\sigma = 2.7927 + 10.11 \exp(-0.01775 T) - 1.417 \exp(-0.01146 T)$ was used [34].

^b The 2B association scheme was applied for all components under investigation (water and all halogenobenzoic acids. The association parameters were inherited from benzoic acid [36]).

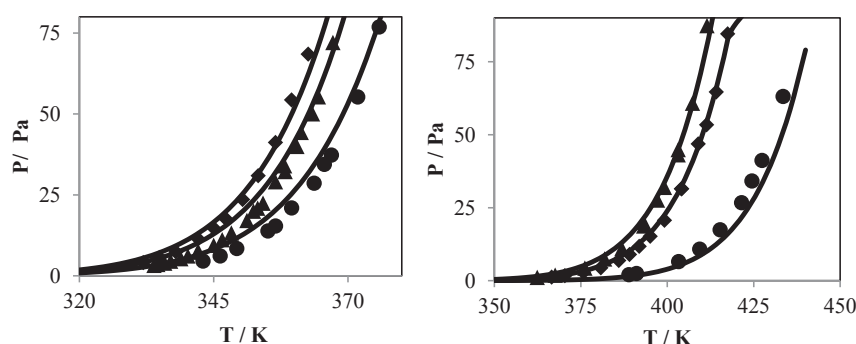


Fig. 1. Absolute vapor pressures P vs. temperature T of pure monohalogenobenzoic acids. Symbols represent experimental data of this work from Table 2 (triangles: 2-halogenobenzoic acid, diamonds: 3-halogenobenzoic acid, circles: 4-halogenobenzoic acid), lines represent PC-SAFT correlation results using parameters from Table 6. Left figure: Fluorobenzoic acids. Right figure: Iodobenzoic acids.

Application of these parameters to model vapor pressures allow for reasonable correlation results of the experimental data. The results of the three-fit parameter estimation are illustrated in Fig. 1. For both, fluorobenzoic acids and iodobenzoic acids PC-SAFT reasonably describes the vapor-pressure curves, and obviously deviations to experimental data are highest for the 4-halogenobenzoic acids. Considering the very low absolute vapor pressures of these substances and the fact that only three parameters were adjusted to the experimental data, PC-SAFT modeled vapor pressures can be considered satisfying.

The deviations between modeled (y_k^{mod}) and experimental data (y_k^{exp}) were calculated according to

$$ARD = 100 \cdot \frac{1}{NP} \cdot \sum_{k=1}^{NP} \left| \left(1 - \frac{y_k^{mod}}{y_k^{exp}} \right) \right| \quad (9)$$

The ARD values for the vapor pressures of the pure

monohalogenobenzoic acids are listed in Table 7. It can be observed that the listed ARD values are in the range of 10–25%. This compares well to modeling results obtained in previous works [27] [Held 2015]. Considering the vapor pressures of the pure compounds, very low experimental absolute pressures can be observed for the 4-halogenobenzoic acids. On the one hand, the reason for this is a very complex and non-ideal behavior, which is difficult to capture with any equation of state. On the other hand (besides numerical difficulties at very low pressures), model deviations from very low absolute pressures cause high relative deviations. This is the reason why the ARD values are usually highest for the 4-halogenobenzoic acids. The obtained ARD values are much higher compared to conventional associating fluids such as solvents (e.g. alcohols). Despite these high ARD values absolute deviations are very small. The maximum deviation for the vapor pressure of 2-fluorobenzoic acid and 3-fluorobenzoic acid in the considered temperature range was found to be about 4 Pa. Thus, the PC-SAFT

Table 7

ARD values for vapor pressures (ARD_p) and solubility (ARD_m) for the monohalogenobenzoic acids investigated in this work.

Compo-nent	2-chloro benzoic acid	3-chloro benzoic acid	4-chloro benzoic acid	2-fluoro benzoic acid	3-fluoro benzoic acid	4-fluoro benzoic acid	2-iodo benzoic acid	3-iodo benzoic acid	4-iodo benzoic acid
Vapor pressures (/Pa) of pure monohalogenobenzoic acids									
T-range vapor pressure	338.1–402.6	348.5–404.1	358.4–398.3	333.9–367.2	331.9–359.5	343–386.2	362.4–411.5	366.6–422	388.9–433.5
ARD_p , %	32.80	19.00	18.40	25.89	14.81	22.37	13.65	9.67	21.66
Solubility (/molality) of monohalogenobenzoic acids in water									
T-range solubility	298.15	298.15	298.15	298.15	298.15	298.15	288.15	288.15	288.15
ARD_m , %	2.6	9.8	26.3	0.5	31.7	11.7	77.5	46.1	72.9

modeling results can be considered to be within the range of uncertainty of the experimental data.

Experimental vapor pressures are ordered in the series 2-iodobenzoic acid > 3-iodobenzoic acid > 4-iodobenzoic acid (Fig. 1) and 2-chlorobenzoic acid > 3-chlorobenzoic acid > 4-chlorobenzoic acid [Held 2015]. Interestingly, experimental vapor pressures are ordered in the series 3-fluorobenzoic acid > 2-fluorobenzoic acid > 4-fluorobenzoic acid (Fig. 1). Although there is no general rule or evidence, the differences of the crystal packing of ortho-, meta-, or para isomers (especially packing with the smallest halogen F) might be responsible for the latter experimental observation. Considering the PC-SAFT parameters in Table 6, modeling this reverse of the series was successful by applying a high dispersion–energy parameter u_i/k_B for 2-fluorobenzoic acid. Whereas u_i/k_B values increase in the order 2-iodobenzoic acid > 3-iodobenzoic acid > 4-iodobenzoic acid and 2-chlorobenzoic acid > 3-chlorobenzoic acid > 4-chlorobenzoic acid, they increase in the order 3-fluorobenzoic acid > 2-fluorobenzoic acid > 4-fluorobenzoic acid. That is, the u_i/k_B series directly follow the series of the experimental vapor pressures. This is an expected result as the association parameters ϵ^{AiBi}/k_B and κ^{AiBi} were set to constant numbers for all benzoic-acid related components in this work (see Table 6).

3.4.2. Solubility in water

Experimental solubility data of monohalogenobenzoic acids is scarcely available in the literature. For chlorobenzoic acids, several researchers reported solubility data at ambient and non-ambient temperatures [Held 2015]. However, solubilities of iodobenzoic acids in water and of fluorobenzoic acids in water were measured at one temperature only. The experimental solubility data collected in Ref. [17] are illustrated in Fig. 2, which presents the solubility of the monohalogenobenzoic acids in moles monohalogenobenzoic acid per kg of pure water, i.e. as molality. Note, that the original data [17] were reported based on the unit scale molarity, i.e. moles monohalogenobenzoic acids per liter solution. Due to the very low solubility of the monohalogenobenzoic acids in water, 1 L solution was assumed to be one kg of pure water at the considered temperature (298.15 K and 288.15 K). The error of this conversion can be estimated to be within the experimental uncertainty of the raw solubility data.

It can be seen from Fig. 2 that the solubility of the fluorobenzoic acids are generally higher than those of the chlorobenzoic acids, and the iodobenzoic acids are almost insoluble in water at 298.15 K.

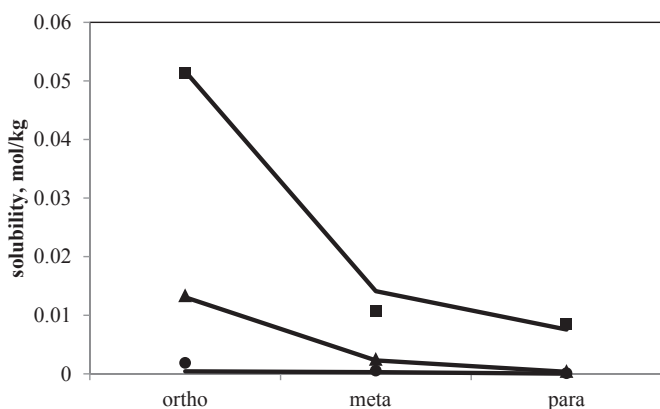


Fig. 2. Solubility of monohalogenobenzoic acids in water at atmospheric pressure. Symbols represent experimental data from literature [17] (squares: fluorobenzoic acids at 298.15 K, triangles: chlorobenzoic acids at 298.15 K, circles: iodobenzoic acids at 288.15 K), lines represent PC-SAFT modeling results using parameters from Table 6.

It can be further observed from the data that the 2-monohalogenobenzoic acids (denoted as ortho in Fig. 2) are more soluble than the 3-monohalogenobenzoic acids (denoted as meta in Fig. 2) and 4-monohalogenobenzoic acids (denoted as para in Fig. 2). Independent of the kind of halogen-substitute, solubility of 3-monohalogenobenzoic acids and 4-monohalogenobenzoic acids is very similar.

These observations are based on data that stem from one single literature source. Thus, it appears promising to validate those data. Besides carrying out more measurements, solubility of the monohalogenobenzoic acids are accessible also by PC-SAFT modeling. In order to validate experimental data, a predictive modeling approach within PC-SAFT is required, that is detached from solubility correlations usually performed with thermodynamic models. Solubility predictions using an equation of state require pure-component parameters (these are available in Table 6 for PC-SAFT) and a solid–liquid equilibrium condition (Eq. (3)) as well as fusion properties (Tables 5 and 6). Setting the binary interaction parameter k_{ij} between water and a monohalogenobenzoic acid equal to zero finally allows predicting the solubility in water. As a result, the PC-SAFT predicted solubilities of the monohalogenobenzoic acids under investigation in water at one temperature are presented in Fig. 2. It becomes obvious that PC-SAFT predicts the solubility data in good agreement with the experimental data. This includes the observations that the solubility of the fluorobenzoic acids are higher than those of the chlorobenzoic acids and the iodobenzoic acids, as well as that the 2-monohalogenobenzoic acids are more soluble than the 3-monohalogenobenzoic acids and 4-monohalogenobenzoic acids, respectively. Note, that the three PC-SAFT parameters σ , m^{seg} and u_i/k_B were fitted solely to the vapor pressures of the monohalogenobenzoic acids. The k_{ij} parameters were set to zero except for 2-chlorobenzoic acid/water and 3-chlorobenzoic acid/water, as these values were available from literature [Held2015]. These k_{ij} values are listed in Table 6.

The deviations between experimental and PC-SAFT predicted solubility are expressed as molality-based ARD_m values and listed in Table 7. Average values of about 15% can be observed for the solubility of chlorobenzoic acids and fluorobenzoic acids. The values for iodobenzoic acids are higher (average about 65%); this is due to the very low solubility of iodobenzoic acids. To give an example, the absolute deviation between experimental and PC-SAFT predicted solubility of 4-iodobenzoic acid is $8 \cdot 10^{-5}$ mol/kg. In sum, the result (shown in Fig. 2 and ARD values listed in Table 7) obtained with the approach is very promising. It can be stated that PC-SAFT might be useful for predictively screening solubility of benzoic acid derivatives given that reliable pure-component PC-SAFT parameters are available.

4. Conclusions

Absolute vapor pressures, sublimation enthalpies and enthalpies of fusion of 2-, 3-, and 4-monohalogenobenzoic acids (halogen = fluorine and iodine) were measured. Combined with thermochemical data from literature these data were used to recommend a set of sublimation and fusion enthalpies for further use in future.

The recommended data set was used to estimate PC-SAFT pure-component parameters. PC-SAFT allowed modeling the vapor pressures of the monohalogenobenzoic acids in good agreement with the experimental data. The experimentally observed reversed order of vapor pressures of 2-fluorobenzoic acid compared to 2-iodobenzoic acid or 2-chlorobenzoic acid was successfully modeled by applying a high dispersion–energy parameter u_i/k_B for 2-fluorobenzoic acid.

The pure-component PC-SAFT parameters were applied to satisfyingly predict the solubility of the monohalobenzoic acids in water at 298.15 K. This approach proved the capability of PC-SAFT to predict solid–liquid phase equilibria if precise data on vapor pressures and fusion properties is available. It can be stated that PC-SAFT might be useful for predictively screening solubility of benzoic acid derivatives given that reliable pure-component PC-SAFT parameters are available. The quality of the pure-component parameters depends on the reliability of the experimental vapor pressures.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.fluid.2015.10.001>.

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