PC-SAFT modeling of CO₂ solubilities in hydrophobic deep eutectic solvents

Citation for published version (APA):

Dietz, C. H. J. T., van Osch, D. J. G. P., Kroon, M. C., Sadowski, G., van Sint Annaland, M., Gallucci, F., Zubeir, L. F., & Held, C. (2017). PC-SAFT modeling of CO₂ solubilities in hydrophobic deep eutectic solvents. *Fluid Phase Equilibria*, 448, 94–98. <https://doi.org/10.1016/j.fluid.2017.03.028>

Document license:
TAVERNE

DOI:
[10.1016/j.fluid.2017.03.028](https://doi.org/10.1016/j.fluid.2017.03.028)

Document status and date:
Published: 25/09/2017

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

PC-SAFT modeling of CO₂ solubilities in hydrophobic deep eutectic solvents

Carin H.J.T. Dietz ^{a,1}, Dannie J.G.P. van Osch ^{b,1}, Maaïke C. Kroon ^{c,**}, Gabriele Sadowski ^d, Martin van Sint Annaland ^a, Fausto Gallucci ^a, Lawien F. Zubeir ^e, Christoph Held ^{d,*}

^a Chemical Process Intensification, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

^b Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry and Institute for Complex Molecular Systems, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

^c Khalifa University of Science and Technology, Petroleum Institute, Chemical Engineering Department, P.O. Box 2533, Abu Dhabi, United Arab Emirates

^d Department of Biochemical and Chemical Engineering, TU Dortmund University, Emil-Figge-Str. 70, 44227 Dortmund, Germany

^e Separation Technology Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 9 February 2017

Received in revised form

29 March 2017

Accepted 30 March 2017

Available online 31 March 2017

Keywords:

Hydrophobic deep eutectic solvents

CO₂ solubilities

PC-SAFT

ABSTRACT

The PC-SAFT ‘pseudo-pure’ approach was used for the modeling of CO₂ solubilities in various hydrophobic deep eutectic solvents (DEEs) for the first time. Only liquid density data were used to obtain the segment number, the temperature-independent segment diameter and the dispersion-energy parameter, as water activities cannot be obtained for hydrophobic substances. VLE data were successfully predicted without the need for any adjustable binary interaction k_{ij} . Thus, solubilities of CO₂ in hydrophobic DEEs could be approximated with the PC-SAFT model using parameters fitted to liquid densities only.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The anthropogenic emissions of greenhouse gases have attracted widespread attention, especially due to global warming. The major contribution to global warming, more than 60%, is caused by the large emissions of CO₂. Therefore, to attenuate climate changes, the capture of CO₂ should be intensively addressed [1]. Various CO₂ capture technologies exist, among others chemical- and physical absorption, which could be applied at industrial scale. Chemical absorption is preferably used at low CO₂ concentrations. This absorption is performed with alkanolamine solutions, which have some major drawbacks such as high energy consumption, high equipment corrosion rates and a large volume required for the absorber [2]. Physical absorption of CO₂ is conducted with solvents

such as dimethylether, propylene glycol and methanol [2]. Many commercial processes are available based on physical absorption. Some examples are the Selexol-, Rectisol-, Purisol-, Morphosorb- and Fluor-processes [2]. Drawbacks of physical absorption include low CO₂ absorption capacity and a higher uptake of small hydrocarbons, which thereby decrease the yield of the CO₂ capture [2].

A more innovative class of solvents used for the capture of CO₂ is ionic liquids (ILs). An IL is the combination of a cation and an anion, which mainly interact via electrostatic forces. The melting temperature of ILs is lower than 100 °C, but preferably even lower than room temperature [3,4]. The advantages of ILs include a low vapor pressure, tunability of chemical and physical properties by choice of the cation/anion combination and high thermal stability [3,4]. In the last decades, research has shown that ILs present high affinity and selectivity towards CO₂ [5]. However, the high production costs of ILs is still a limiting factor hampering their use at industrial scale.

An interesting, especially cheaper, alternative solvent to ILs are deep eutectic solvents (DEEs). A DEE is the combination of two or more solids, which liquefy upon mixing due to attractive interactions. These attractive interactions consist of hydrogen bonding between the constituents of the DEE in addition to van der

* Corresponding author.

** Corresponding author.

E-mail addresses: m.c.kroon@tue.nl, mkroon@pi.ac.ae (M.C. Kroon), christoph.held@bci.tu-dortmund.de (C. Held).

¹ These authors contributed equally.

Waals interactions [6]. The main advantage of DESs is their tunability in thermal, physical and chemical properties by changing both the constituents and their mixing ratio [6]. Furthermore, they are relatively easy to make (by simply mixing both constituents upon heating) and therefore their production is generally cheaper than ILs and other innovative solvents.

In 2008, CO₂ capture with hydrophilic DESs was presented for the first time. In this work, the DES composed of urea and choline chloride was used [7]. Although CO₂ capture in hydrophilic DESs was found to be promising, the capacity was still not comparable to ILs. Later on, in 2015, hydrophobic DESs were discovered, which were subsequently successfully used for the removal of fatty acids, biomolecules and metal ions from water [8–10]. Recently, also CO₂ solubilities in hydrophobic DESs were measured [11]. The solubility of CO₂ in these hydrophobic DESs was higher than in the hydrophilic DESs and even comparable to some of the best performing ILs. However, there are many different hydrophobic DESs possible (tunability) and experiments for the selection of the best performing DESs are time-consuming. Thus, it is extremely important to develop robust models able to predict CO₂ solubilities in hydrophobic DESs.

Recently, CO₂ solubilities in hydrophilic DESs have been modeled with Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [12]. In that work, two different modeling strategies were compared, the ‘pseudo-pure’ component approach and the individual-component approach [12]. In the ‘pseudo-pure’ component approach, the DES is considered as one component, despite the fact that it is actually constituted by two or more components. In the individual-component approach, the individual components of the DESs are modeled separately to attain the pure component parameters. These parameters were obtained by fitting densities of the aqueous solution of the pure components. The advantage of the ‘individual-component’ approach is its physical consistency, allowing prediction of the CO₂ solubilities in hydrophilic DESs at different molar ratios. Instead, the ‘pseudo-pure’ component approach requires different parameters for every DES, but is a more simple and pragmatic method. The pure-component parameters for the ‘individual-component’ approach are usually obtained by fitting to pure-component data or to data of the aqueous solution of the pure components. Most of the DES constituents considered in this work are solid at ambient conditions and very hydrophobic (water insoluble). Thus, pure-component parameters could not be obtained. Therefore, the individual-component approach could not be applied. For that reason the ‘pseudo-pure’ component strategy is more convenient for modeling CO₂ solubilities in hydrophobic DESs [12].

In this work, PC-SAFT was used to model the CO₂ solubility of the following four hydrophobic DESs and one DES/IL mixture: (i) decanoic acid-tetraoctylammonium chloride in a 2-1 ratio (DecA-N₈₈₈₈-Cl (2:1)), (ii) decanoic acid-tetraoctylammonium chloride in a 1.5-1 ratio (DecA-N₈₈₈₈-Cl (1.5:1)), (iii) decanoic acid-tetraoctylammonium bromide in a 2-1 ratio (DecA-N₈₈₈₈-Br

(2:1)), (iv) decanoic acid-tetrabutylammonium chloride in a 2-1 ratio (DecA-N₄₄₄₄-Cl (2:1)), and (v) perfluorodecanoic acid-tetraoctylammonium chloride in a 2-1 ratio (PerFDecA-N₈₈₈₈-Cl (2:1)), for which we have recently reported the experimental data in the literature, which were obtained by using a gravimetric method [11]. It should be mentioned that PerFDecA-N₈₈₈₈-Cl (2:1) is actually partially ionized and so to some extent an IL rather than a DES.

2. Modeling

PC-SAFT has been first introduced by Gross and Sadowski [13,14]. It is based on statistical thermodynamics from Barker and Henderson in 1967 [15,16]. PC-SAFT is a perturbation theory, which accounts for association and dispersive forces. SAFT commonly calculates the residual Helmholtz energy based on the difference between the total molar Helmholtz energy and the Helmholtz energy of an ideal gas. In PC-SAFT the residual molar Helmholtz energy is calculated by the sum of hard-chain interactions, energy contribution due to dispersion forces and site-site specific bonding interactions. For more information regarding PC-SAFT, the corresponding formulas and the modeling of gas solubilities an interested reader is referred to previous works [13,14].

The pure component parameter estimation and the applied modeling strategy was inherited from Zubeir et al with the understanding that only the pseudo-pure modeling strategy is used in this work [12]. This strategy is briefly summarized here. The estimated parameters are: the segment number ($m_{\text{seg},i}$), the temperature-independent segment diameter (σ_i), the dispersion-energy parameter (u_i/k_B), the association-energy parameter ($\epsilon^{\text{AiBi}}/k_B$) and the effective volume of an association site (κ^{AiBi}). As these parameters were not available in literature, they were estimated in this work by fitting to experimental liquid density data from literature [8]. In contrast, the association-energy parameter ($\epsilon^{\text{AiBi}}/k_B$) and the effective volume of an association site (κ^{AiBi}) were not fitted to density data, as density data is inappropriate for fitting these association parameters. Thus, they were set to constant values according to suggestions from previous works [17–20]. For the formation of the DES, self-association via hydrogen bonding between the hydrogen bond acceptor (HBA) and the hydrogen bond donor (HBD) was considered. Thus, two association sides were accredited to the DES. The average molar mass of the studied DESs was calculated from the molar masses of the individual components and their molar ratio (see Table 1).

3. Results and discussion

3.1. PC-SAFT parameters and density correlation

Table 1 shows the results for the pure component parameters of CO₂ and the DESs. The pure-component PC-SAFT parameters for CO₂ were obtained from literature [18]. For the hydrophobic DESs,

Table 1

PC-SAFT pure component parameters for CO₂ and DESs. The parameters for CO₂ and the two hydrophilic DESs were obtained from literature [12,18].

Compounds	$M_w/\text{g} \cdot \text{mol}^{-1}$	$m_{\text{seg},i}$	$\sigma_i/\text{\AA}$	u_i/k_B (K)	N_{site}	$\epsilon^{\text{AiBi}}/k_B$ (K)	κ^{AiBi}
CO ₂ [18]	44.01	2.0727	2.7852	169.21	1 + 1	0	0.1
DecA-N ₈₈₈₈ -Cl (2:1)	282.22	15.322	3.1533	307.11	1 + 1	5000	0.1
DecA-N ₈₈₈₈ -Cl (1.5:1)	304.23	14.800	3.2400	382.09	1 + 1	5000	0.1
DecA-N ₈₈₈₈ -Br (2:1)	297.04	15.482	3.1583	317.42	1 + 1	5000	0.1
PerFDecA-N ₈₈₈₈ -Cl (2:1)	510.17	31.855	2.585	219.95	1 + 1	5000	0.1
DecA-N ₄₄₄₄ -Cl (2:1)	207.41	10.908	3.1535	311.30	1 + 1	5000	0.1
LA:TBA-Cl (2:1) ¹²	152.69	11.7300	2.6760	303.76	1 + 1	5000	0.1
LA:TBA-Cl (3:1) ¹²	137.04	10.5328	2.6760	338.00	1 + 1	5000	0.1

Fig. 1. Densities of PerFDecA:N₈₈₈-Cl (2:1), DecA:N₈₈₈-Br (2:1), DecA:N₄₄₄-Cl (2:1), DecA:N₈₈₈-Cl (2:1) and DecA:N₈₈₈-Cl (1.5:1), as function of the temperature. The symbols represent the experimental data and the solid lines represent the PC-SAFT results using the parameters from Table 1.

N_{site} was set to $1 + 1$, $\epsilon^{\text{AiBi}}/k_B$ to 5000 and κ^{AiBi} to 0.1. Induced association according to Kleiner and Sadowski [21] was applied for CO₂+DES mixtures. The pure component parameters, $m_{\text{seg},i}$, σ_i , and u_i/k_B , of the designated DESs were fitted to their liquid densities available in the literature [8]. The results of these fits are shown in Fig. 1. They show slight overestimation at low temperatures and slight underestimation at high temperatures. The absolute average relative deviation, AARD (%), between experimental densities of the DESs and the DES/IL system in combination with the PC-SAFT correlation are listed in Table 2. The AARD (%) show values not higher than 0.150, which is a good agreement between the densities determined via experiments and PC-SAFT. Table 1 shows comparison of PC-SAFT parameters for hydrophilic DESs with the hydrophobic DESs determined in this work. It can be observed that the three pure component PC-SAFT parameters ($m_{\text{seg},i}$, σ_i , and u_i/k_B) are in the same order of magnitude for the hydrophobic and hydrophilic DESs. An exception can be found for PerFDecA-N₈₈₈-Cl, which has a very high number of segments $m_{\text{seg},i}$. This can be expected due to the higher molar mass of PerFDecA-N₈₈₈-Cl compared to the DESs.

Equation (1) shows the calculation for the AARD (%) between the experimental and the modeled densities.

$$\text{AARD}(\%) = \frac{1}{n} \sum \left| \frac{y_i^{\text{exp}} - y_i^{\text{calc}}}{y_i^{\text{calc}}} \right| \cdot 100 \quad (1)$$

In this equation y is a property determined via experiments and modeling of component i , while n is the number of experimental data points.

Fig. 2 shows the correlation between the molar mass (M_w) of the

Fig. 2. Correlation between the molecular weight (M_w) and the segment volume ($m_{\text{seg}} \cdot \sigma^3$) obtained with PC-SAFT from Table 1 for hydrophobic DESs modeled in this work and hydrophilic DESs modeled elsewhere [12].

DESs and their segment volume ($m_{\text{seg}} \cdot \sigma^3$). The higher the M_w of the DES, the higher $m_{\text{seg}} \cdot \sigma^3$. For comparison, the hydrophilic DESs modeled by Zubeir et al. [12] are also included in Fig. 2. With exclusion of PerFDecA:N₈₈₈-Cl (2:1), a strong linear correlation with an R^2 of 0.9931 between the molar mass of the DESs and their segment volume is obtained. When PerFDecA:N₈₈₈-Cl (2:1) was also considered, the correlation was not linear. A plausible explanation for the exclusion of PerFDecA:N₈₈₈-Cl (2:1) can be justified by the reaction that occurs, leading to partial ionization and therefore to some extent the formation of an IL.

3.2. CO₂ solubility in hydrophobic DESs

Based on the PC-SAFT parameters listed in Table 1, CO₂ solubilities were predicted in the considered hydrophobic DESs. For all DESs, the VLE data of the binary DES + CO₂ systems were predicted without adjusting any binary interaction parameter. Table 3 shows the percentage AARD (%) between the experimental and the predicted VLE of the DES + CO₂ systems, which was determined with equation (1). Fig. 3A–E show the VLE data of all hydrophobic DESs + CO₂ systems studied in this work.

The predictions of PC-SAFT for the DES DecA:N₈₈₈-Cl (2:1) + CO₂ show a good comparison with the experimental data at

Table 3

Absolute average relative deviation, AARD (%), of the VLE data at various temperatures for the examined DES + CO₂ systems.

System	T (K)	No. of data points	k_{ij}	AARD (%)
DecA-N ₈₈₈ -Cl (2-1) + CO ₂	298.15	12	0	4.01
	308.15	12		4.67
	323.15	12		7.93
DecA-N ₈₈₈ -Br (2-1) + CO ₂	298.15	9	0	12.01
	308.15	9		7.37
	323.15	9		4.15
DecA-N ₄₄₄ -Cl (2-1) + CO ₂	298.15	12	0	3.92
	308.15	12		7.60
	323.15	12		10.94
DecA-N ₈₈₈ -Cl (1.5–1) + CO ₂	298.15	9	0	8.70
	308.15	12		5.08
	323.15	12		2.27
PerFDecA-N ₈₈₈ -Cl + CO ₂	298.15	11	0	3.96
	308.15	11		4.43
	323.15	11		5.00

Table 2

Absolute average relative deviation, AARD (%), between experimental densities and PC-SAFT modeling pure DESs within the temperature range of 288.15–323.15 K.

System	No. of data point	AARD (%)
DecA-N ₈₈₈ -Cl (2-1)	8	0.150
DecA-N ₈₈₈ -Br (2-1)	8	0.103
DecA-N ₄₄₄ -Cl (2-1)	8	0.008
DecA-N ₈₈₈ -Cl (1.5–1)	8	0.135
PerFDecA-N ₈₈₈ -Cl	8	0.123

Fig. 3. VLE of different hydrophobic DES + CO₂ systems at three isotherms. (diamonds: 298.15, circles: 308.15 and squares: 323.15 K) [11]. The lines are results obtained with PC-SAFT using the parameters in Table 1. The following DESs are shown: (A) DecA:N₈₈₈₈-Cl (2:1) + CO₂; (B) DecA:N₈₈₈₈-Cl (1.5:1) + CO₂; (C) DecA:N₈₈₈₈-Br (2:1) + CO₂; (D) PerF-DecA:N₈₈₈₈-Cl (2:1) + CO₂; (E) DecA:N₄₄₄₄-Cl (2:1) + CO₂.

a temperature of 298.15 K and 308.15 K with an AARD (%) of 4.01% and 4.67%, respectively [11]. At 323.15 K the PC-SAFT underestimates the system pressure of DES + CO₂ system resulting in a higher AARD (%) of 7.93%. For the 1.5:1 molar ratio of the DES DecA:N₈₈₈-Cl the predictions at 308.15 K and 323.15 K are reasonable to good with AARD (%) values of 5.08% and 2.27%, respectively. At 298.15 K the model slightly overestimates the experimental pressure. PC-SAFT overestimated the isotherms for the DecA:N₈₈₈-Br (2:1) + CO₂ system. The overestimation increased with temperature. For the PerFDecA:N₈₈₈-Cl (2:1) good agreement is obtained, but PC-SAFT overestimates the experimental pressure for all temperatures. The lower the temperature is, the higher the overestimation. PC-SAFT underestimates the CO₂ solubilities in the DES DecA:N₄₄₄-Cl (2:1), where the AARD (%) increases for increasing temperatures.

4. Conclusions

It is shown for the first time that PC-SAFT can be used for the modeling of the solubility of CO₂ in hydrophobic DESs using the 'pseudo-pure' approach. The PC-SAFT model shows a quite reasonable correlation between the experimental and modeled densities, which served in this work as input to the estimation of the PC-SAFT parameters. The segment number (m_{seg}), the temperature-independent segment diameter (σ), and the dispersion-energy parameter (u/k_B) were only fitted to liquid densities of the hydrophobic DESs, while the association parameters were set to constant values using the 2B association scheme. The CO₂ solubility could be predicted reasonably well for all systems under investigation. That is, binary interaction parameters were not used. These results are promising, and they prove that PC-SAFT can be used in a very pragmatic approach to screen DESs for prediction of CO₂ solubilities in them. This means significant time saving compared to experimental methods.

Acknowledgements

This work was performed under the framework of Chemelot InSciTe and with contributions from the European Regional Development Fund (ERDF) within the framework of OP-Zuid and with contributions from the province of Brabant and Limburg and the Dutch ministry of economy. Furthermore the authors would

like to thank the members of the ISPT "Deep Eutectic Solvents in the pulp and paper industry" consortium for their financial and in kind contribution. This cluster consists of the following organisations: Altri – Celbi, Buckman, Crown Van Gelder, CTP, DS Smith Paper, Eska Graphic Board, Holmen, ISPT, Mayr-Melnhof, Metsä Fibre, Mondi, Omya, Parenco BV, Portucel, Sappi, SCA, Smurfit Kappa, Stora Enso, Eindhoven University of Technology, University of Aveiro, University of Twente, UPM, Van Houtum, Voith Paper, VTT Technical Research Centre of Finland Ltd and Zellstoff Pöls. Furthermore, this project received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement Provides No. 668970.

References

- [1] J. Albo, P. Luis, A. Irabien, *Ind. Eng. Chem. Res.* 49 (2010) 11045–11051.
- [2] C.-H. Yu, C.-H. Huang, C.-S. Tan, *Aerosol Air Qual. Res.* 12 (2012) 745–769.
- [3] J.P. Hallett, T. Welton, *Chem. Rev.* 111 (2011) 3508–3576.
- [4] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, vol. 1, Wiley Online Library, 2008.
- [5] J.L. Anthony, J.L. Anderson, E.J. Maginn, J.F. Brennecke, *J. Phys. Chem. B* 109 (2005) 6366–6374.
- [6] M. Francisco, A. van den Bruinhorst, M.C. Kroon, *Angew. Chem. Int. Ed. Engl.* 52 (2013) 3074–3085.
- [7] X. Li, M. Hou, B. Han, X. Wang, L. Zou, *J. Chem. Eng. Data* 53 (2008) 548–550.
- [8] D.J.G.P. van Osch, L.F. Zubeir, A. van den Bruinhorst, M.A.A. Rocha, M.C. Kroon, *Green Chem.* 17 (2015) 4518–4521.
- [9] D.J.G.P. van Osch, D. Parmentier, C.H.J.T. Dietz, A. van den Bruinhorst, R. Tuinier, M.C. Kroon, *Chem. Commun.* 52 (2016) 11987–11990.
- [10] B.D. Ribeiro, C. Florindo, L.C. Iff, M.A. Coelho, I.M. Marrucho, *ACS Sustain. Chem. Eng.* 3 (2015) 2469–2477.
- [11] L.F. Zubeir, D.J.G.P. van Osch, M.A.A. Rocha, F. Banat, M.C. Kroon, *J. Phys. Chem. B* (2017).
- [12] L.F. Zubeir, C. Held, G. Sadowski, M.C. Kroon, *J. Phys. Chem. B* 120 (2016) 2300–2310.
- [13] J. Gross, G. Sadowski, *Ind. Eng. Chem. Res.* 41 (2002) 5510–5515.
- [14] J. Gross, G. Sadowski, *Ind. Eng. Chem. Res.* 40 (2001) 1244–1260.
- [15] J.A. Barker, D. Henderson, *J. Chem. Phys.* 47 (1967) 2856–2861.
- [16] J.A. Barker, D. Henderson, *J. Chem. Phys.* 47 (1967) 4714–4721.
- [17] L.F. Zubeir, M.H. Lacroix, M.C. Kroon, *J. Phys. Chem. B* 118 (2014) 14429–14441.
- [18] X. Ji, C. Held, G. Sadowski, *Fluid Phase Equilib.* 335 (2012) 64–73.
- [19] A.P. Carneiro, O. Rodríguez, C. Held, G. Sadowski, E.A. Macedo, *J. Chem. Eng. Data* 59 (2014) 2942–2954.
- [20] V.N. Emel'yanenko, D.H. Zaitsau, E. Shoifet, F. Meurer, S.P. Verevkin, C. Schick, C. Held, *J. Phys. Chem. A* 119 (2015) 9680–9691.
- [21] M. Kleiner, G. Sadowski, *J. Phys. Chem. C* 111 (2007) 15544–15553.