Journal of chemical & engineering data

Article

pubs.acs.org/jced

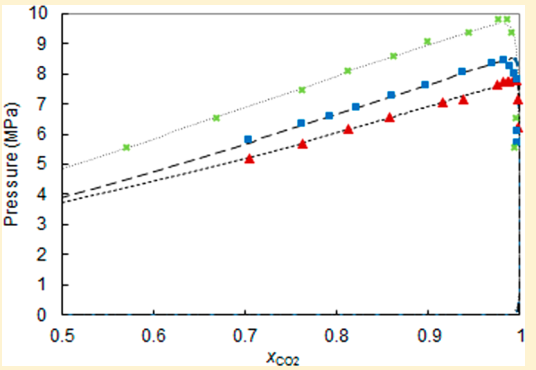
Experimental Determination and Modeling of the Phase Behavior of the CO_2 + Propionic Anhydride Binary System at High Pressure

Sílvia Rebocho,[†] Ana V. M. Nunes,[†] Vesna Najdanovic-Visak,[‡] Susana Barreiros,[†] and Alexandre Paiva*[,†]

[†]LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal

[‡]Energy Lancaster, Engineering Department, Lancaster University, Lancaster LA1 4YR, United Kingdom

ABSTRACT: The phase equilibrium of the binary system (CO_2 + propionic anhydride) was determined experimentally at temperatures of 308, 313, and 323 K and pressures up to 10 MPa. Measurements were carried out in a high-pressure visual cell with variable volume. The experimental data were modeled using the Peng−Robinson equation of state and the Mathias−Klotz−Prausnitz mixing rule. A good correlation was achieved with this model, with a total average absolute deviation of 0.21%.



INTRODUCTION

Propionic anhydride is a simple acid anhydride, highly reactive and therefore widely used in organic synthesis for the production of dyes, pharmaceuticals, agrochemicals, and fragrance chemicals.[1−3] It is produced from the dehydration of propionic acid, an important candidate to C_3 platform chemical, as it can be derived from biomass[4] or biosynthesized.[5] This possibility opens up renewed opportunities of applications for both propionic acid and its anhydride.

As part of the ongoing interest in exploring CO_2 as solvent for the enzymatic resolution of sec-alcohols, using propionic anhydride as the acylating agent, we report here the phase behavior of the binary system CO_2 + propionic anhydride. To the best of our knowledge, this is the first time that the phase behavior of CO_2 + propionic anhydride is reported in literature.

Supercritical CO_2 ($scCO_2$) is an attractive medium in which to perform and control biocatalytic reactions.[6−9] Moreover, it has the potential to provide considerable improvements to the sustainability of a process, mainly due to its nonflammability, low toxicity, and high availability.[10] The application of $scCO_2$ to chemical processes, allows to partially or totally eliminate the use of organic solvents, to integrate product separation steps and to enable catalyst reutilization. On the other hand, $scCO_2$ can decrease mass transfer limitations by decreasing viscosity and increasing diffusivity of reaction systems, or even totally remove phase barriers when above the critical line of the mixture. In fact, with manipulation of operation conditions, it is possible to perform reactions in high pressure CO_2 in a single phase system or in a two phase system.[11] Although faster reaction rate can be normally achieved in a single phase system, biphasic systems can in some circumstances present some advantages when integrating reaction/separation or when the removal of one the product favors product formation.[12−14] Finally, some authors have manage to change selectivity by manipulating the phase state of a reaction,[14] while others have manage to develop fully integrated continuous process with product recover.[15−18]

In this work, high-pressure measurements were carried out at temperatures of 308, 313, and 323 K, in a pressure range from 5 to 10 MPa. These data were fitted with the Peng−Robinson equation of state (PR EOS)[19] and with the Mathias−Klotz−Prausnitz (MKP)[20] mixing rule. The capability of the model was tested in the correlation of the phase behavior of the binary system with the multicomponent mixtures of the experimental data, using the program package PE2000 developed by Pfohl et al.[21]

EXPERIMENTAL SECTION

Materials. The specifications of chemicals used in this work are presented in Table 1. Propionic anhydride (≥99%), CAS [123-62-6], was supplied by Sigma-Aldrich, and carbon dioxide (N48, with a high purity of 99.998 mol %), CAS [124-38-9], was supplied by Air Liquid. The chemicals were used as received, without any further purification.

Table 1. Specifications of Chemicals Used in This Study

chemical name	source	certified purity
propionic anhydride	Sigma-Aldrich	≥99%
CO_2	Air Liquid	99.998 mol %

Received: July 6, 2016
Accepted: November 16, 2016

DOI: 10.1021/acs.jced.6b00595
J. Chem. Eng. Data XXXX, XXX, XXX−XXX

Apparatus. Phase equilibria experiments were carried out in a high-pressure apparatus, from New Ways of Analytics GmbH (Germany). The experimental apparatus is described elsewhere.[22] In summary, the visual cell is composed by two sapphire windows, on both sides of the cell. This allows for the observation of any phase transition. The internal volume of the cell is controlled by moving the sapphire window placed on the back of the cell, which acts as a piston. This is accomplished by using a hydraulic fluid pump. The viewing cell has an internal volume of 38−70 mL and can operate at temperatures up to 453 K and at pressures up to 70 MPa. The control of temperature is achieved with a PID controller (Eurotherm 2216e) (Pt100, 1/16 Din). The temperature is measured directly from the fluid inside the cell with an accuracy of 0.1 K. Pressure is measured by an Omega DP41-E230 transducer with an accuracy of ±0.005% RDG. Mixing inside the cell is achieved with a magnetically coupled stirrer.

Experimental Methods. Experimental measurements were performed using the static synthetic method, with phase transitions being visually determined by the appearance of a new phase (dew/bubble point) when slowly decompressing a homogeneous mixture of known composition.

To each composition, specific quantities of propionic anhydride and CO_2 were loaded into the cell. Briefly, the cell is loaded with the propionic anhydride (solute) with the help of a syringe. The syringe with the solute was weighed before and after loading the cell, to determine the weight of the solute that was placed inside the cell. The uncertainty associated with the solute measurements is ±0.002 g. CO_2 was then added by means of a manual screw pump at a temperature of 273 K and its amount controlled by means of volume variation in each rotation, as described by Podila et al.[22] The volume variation of each rotation has been previously calibrated. To determine the amount of CO_2 loaded into the cell, CO_2 densities were calculated using the Span and Wagner EOS.[23] The uncertainty in the composition was estimated to be ±0.005 mole fraction.

After reaching the desired experimental temperature, the cell was pressurized by moving the back sapphire piston forward. After the system reaches a single phase, stirring is maintained for 30 min. At this point, stirring is stopped, and pressure is decreased moving the piston backward until the first bubble/drop is observed (formation of a second phase). Each experimental point is an average of at least four measurements. The uncertainty in pressure is less than 0.05 MPa. The experimental data has an average absolute deviation of 3.5%.

RESULTS AND DISCUSSION

Table 2 shows the experimental data obtained for the bubble and dew points of the (CO_2 + propionic anhydride) binary system at 308, 313, and 323 K and pressures ranging from 5 to 10 MPa. These results are further illustrated in Figure 1. As it was to be expected as pressure increases, the solubility of $scCO_2$ in propionic anhydride increases, and the solubility of propionic anhydride in $scCO_2$ also increases. The same is observed with decreasing temperature. Because no experimental data on the phase behavior of CO_2 + propionic anhydride is available elsewhere, it is impossible to compare with literature.

Propionic anhydride is here presented as an alternative acylating agent in (trans)esterification enzymatic reactions in $scCO_2$ media. Therefore, it is important to compare the solubility of $scCO_2$ in propionic anhydride with the solubility in similar acylating agents such as propionic acid[24] and methyl propionate,[25] commonly used in this type of reactions. The comparison is presented in Figure 2. It can be observed that CO_2 has a higher affinity toward methyl proprionate followed by propionic anhydride and propionic acid. It is also interesting to notice that the affinity of CO_2 to propionic anhydride is very similar to propionic acid. Although differences in solubility are more pronounced at lower pressures (less than 7 MPa), near the critical point of the mixture, the solubility of $scCO_2$ in both compounds is basically the same. The higher affinity of CO_2 toward methyl propionate was to be expected due to its lower polarity when compared with the other two.

Thermodynamic Modeling. The VLE data for CO_2 + propionic anhydride system was correlated with the PR-MKP model. The interaction parameters were calculated by minimizing the deviations between the calculated and the experimental data. The absolute average deviation (AAD)

Table 2. Experimental High-Pressure Phase Equilibrium of the Binary System CO_2 (1) + Propionic Anhydride (2) Expressed in Mole Fraction of Carbon Dioxide (χ_{CO2})[a]

T/K	P/MPa	χ_{CO2}	phase transition[b]
308	5.21	0.7052	BP
	5.66	0.7625	BP
	6.17	0.8128	BP
	6.21	0.9983	DP
	6.55	0.8578	BP
	7.03	0.9159	BP
	7.17	0.9373	BP
	7.17	0.9974	DP
	7.66	0.9752	BP
	7.72	0.9808	BP
	7.75	0.9885	BP
	7.75	0.9857	BP
	7.76	0.9961	DP
	7.78	0.9926	BP
313	5.66	0.9974	DP
	5.76	0.7052	BP
	6.07	0.9979	DP
	6.34	0.7625	BP
	6.55	0.7934	BP
	6.86	0.8221	BP
	7.24	0.8615	BP
	7.59	0.8985	BP
	7.79	0.9977	DP
	8.00	0.9943	BP
	8.03	0.9373	BP
	8.21	0.9900	DP
	8.30	0.9699	BP
	8.41	0.9839	BP
323	5.55	0.5704	DP
	5.55	0.9942	DP
	6.55	0.6677	DP
	6.55	0.9947	DP
	7.48	0.7625	DP
	8.10	0.8117	DP
	8.59	0.8615	DP
	9.10	0.8985	DP
	9.38	0.9903	DP
	9.38	0.9430	DP
	9.79	0.9752	BP
	9.81	0.9857	BP

[a]Estimated uncertainties u are $u(T)$ = 0.1 K $u(p)$ = 0.05 MPa and $x(CO_2)$ = 0.005. [b]BP − bubble point; DP − dew point.

DOI: 10.1021/acs.jced.6b00595
J. Chem. Eng. Data XXXX, XXX, XXX−XXX

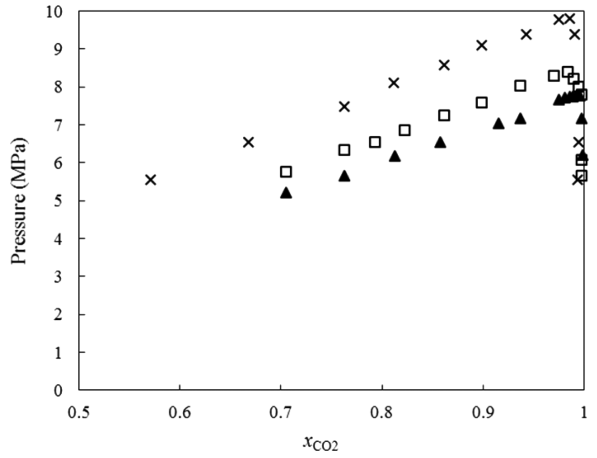


Figure 1. Comparison of VLE data for the CO_2/propionic anhydride binary system at 308 K (▲), 313 K (□), and 323 K (×).

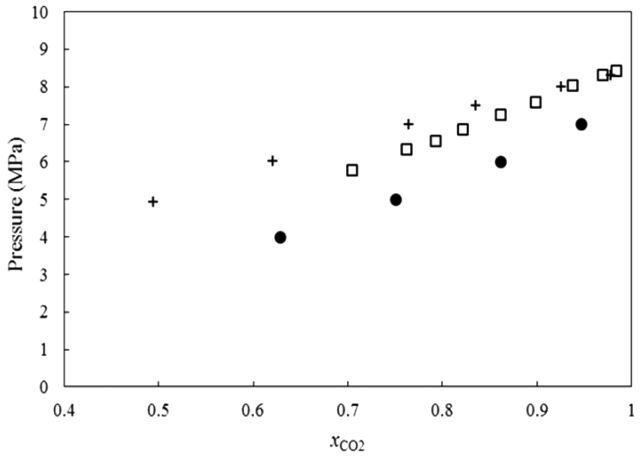


Figure 2. Comparison of the solubility of carbon dioxide in methyl propionate[25] (●), propionic anhydride from this work (□), and propionic acid (+).[24]

between the calculated and the experimental data was determined using eq 1.

$$\mathrm{AAD} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(z_i^{\mathrm{exp}} - z_i^{\mathrm{EOS}})^2} \quad (1)$$

with $z = x$, y and n = number of data.

Critical temperature (T_c), critical pressure (p_c), and acentric factor (ω) of the pure components, presented in Table 3, were used to determine the parameters K_{ij}, l_{ij} and λ_{ij}.

Table 3. Pure Compound Physical Properties[26]

compound	T_c/K	P_c/MPa	ω
propionic anhydride	623	3.27	0.560
CO_2	304.1	7.38	0.239

The optimum binary interaction parameters obtained and the respective AAD values are given in Table 4. As can be observe in Figure 3, the PR-EOS/MKP-MR model is in good agreement to the experimental pT_{xy} data. An AAD of 0.21% was obtained.

Table 4. Optimized Interaction Parameters for the CO_2/Propionic Anhydride Binary System at 308 K (▲), 313 K (□), and 323 K (×) with the Peng–Robinson EOS and the Mathias–Klotz–Prausnitz Mixing Rule

T/K	308	313	323
K_{ij}	0.0217	−0.1081	−0.4191
l_{ij}	−0.0157	−0.0949	−0.3464
λ_{ij}	0.0301	−0.1555	−0.6083
$AAD_{(liquid\ phase)}$ (%)	0.008	0.243	0.148
$AAD_{(gas\ phase)}$ (%)	0.090	0.155	0.366

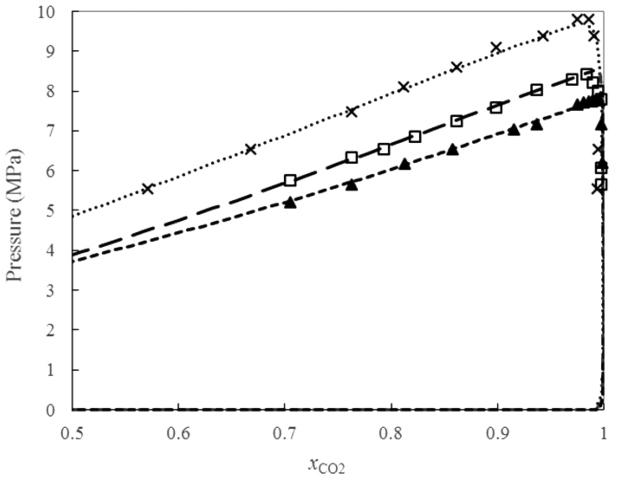


Figure 3. Fitting of the $pTxy$ experimental data (symbols) for the CO_2/propionic anhydride binary system by the PR-EOS/MKP-MR model (lines) 308 K (▲), 313 K (□), and 323 K (×).

CONCLUSION

In this work the phase behavior for the system CO_2 + propionic anhydride was determined, showing that both the solubility of $scCO_2$ in the liquid phase as the solubility of propionic anhydride increased with increasing pressure and decreasing temperature. The experimental data were fitted with the PR-EOS/MKP-MR model, and an excellent correlation was obtained with a total AAD value of 0.21%.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +351 212949680. E-mail address: abp08838@fct.unl.pt (Alexandre Paiva).

ORCID

Sílvia Rebocho: 0000-0003-0559-0823

Funding

The authors would like to express a special thanks to Fundação para a Ciência e Tecnologia – FCT (Portugal) through the Project PTDC/EQU-EQU/122106/2010 and the contract: LAQV, REQUIMTE-UID/QUI/50006/2013. A.V.M.N. and S.R. are thankful to FCT (Portugal) through IF/01374/2014 and SFRH/BD/64133/2009. V.N.-V. is thankful to the Faculty of Science and Technology (Lancaster University, UK) for the research Grant EGA7815.

Notes

The authors declare no competing financial interest.

DOI: 10.1021/acs.jced.6b00595
J. Chem. Eng. Data XXXX, XXX, XXX–XXX

REFERENCES

(1) Gunes, H. H.; Okudan, A. Characterization and dual functionalization of polystyrene with propionic anhydride and cyanate derivatives. *J. Appl. Polym. Sci.* **2013**, *130*, 1351−1362.

(2) Jiang, S.-S.; Xu, Q.-C.; Zhu, M.-Y.; Yu, X.; Deng, W.-P. Kinetic Resolution of alpha-Methylene-beta-hydroxy Esters Catalyzed by Acyl Transfer Catalyst An-PIQ. *J. Org. Chem.* **2015**, *80*, 3159−3169.

(3) Santayanon, R.; Wootthikanokkhan, J. Modification of cassava starch by using propionic anhydride and properties of the starch-blended polyester polyurethane. *Carbohydr. Polym.* **2003**, *51*, 17−24.

(4) Jiang, L.; Cui, H. Y.; Zhu, L. Y.; Hu, Y.; Xu, X.; Li, S.; Huang, H. Enhanced propionic acid production from whey lactose with immobilized *Propionibacterium acidipropionici* and the role of trehalose synthesis in acid tolerance. *Green Chem.* **2015**, *17*, 250−259.

(5) Werpy, T.; Petersen, G. *Top value added chemicals from biomass, Vol. 1 - Results of screening for potential candidates from sugars and synthesis gas*; U.S. Department of Energy: Oak Ridge, TN, 2004.

(6) Mesiano, A. J.; Beckman, E. J.; Russell, A. J. Supercritical biocatalysis. *Chem. Rev.* **1999**, *99*, 623−633.

(7) Matsuda, T.; Harada, T.; Nakamura, K. Biocatalysis in supercritical CO_2. *Curr. Org. Chem.* **2005**, *9*, 299−315.

(8) Hobbs, H. R.; Thomas, N. R. Biocatalysis in supercritical fluids, in fluorous solvents, and under solvent-free conditions. *Chem. Rev.* **2007**, *107*, 2786−2820.

(9) Matsuda, T. Recent progress in biocatalysis using supercritical carbon dioxide. *J. Biosci Bioeng.* **2013**, *115*, 233−241.

(10) Beckman, E. J. Supercritical and near-critical CO_2 in green chemical synthesis and processing. *J. Supercrit. Fluids* **2004**, *28*, 121−191.

(11) Nunes da Ponte, M. Phase equilibrium-controlled chemical reaction kinetics in high pressure carbon dioxide. *J. Supercrit. Fluids* **2009**, *47*, 344−350.

(12) Chouchi, D.; Gourgouillon, D.; Courel, M.; Vital, J.; Nunes da Ponte, M. The influence of phase behavior on reactions at supercritical conditions: The hydrogenation of alpha-pinene. *Ind. Eng. Chem. Res.* **2001**, *40*, 2551−2554.

(13) Nunes, A. V. M; Nunes da Ponte, M. Phase equilibrium and kinetics of O-2-oxidation of limonene in high pressure carbon dioxide. *J. Supercrit. Fluids* **2012**, *66* (66), 23−28.

(14) Montoya, C. A.; Paninho, A. B.; Felix, P. M.; Zakrzewska, M. E.; Vital, J.; Najdanovic-Visak, V.; Nunes, A. V. M Styrene carbonate synthesis from CO_2 using tetrabutylammonium bromide as a non-supported heterogeneous catalyst phase. *J. Supercrit. Fluids* **2015**, *100* (100), 155−159.

(15) Licence, P.; Gray, W. K.; Sokolova, M.; Poliakoff, M. Selective monoprotection of 1.n-terminal Diols in Supercritical carbon dioxide: A striking example of solvent tunable desymmetrization. *J. Am. Chem. Soc.* **2005**, *127*, 293−298.

(16) Paiva, A.; Vidinha, P.; Angelova, M.; Rebocho, S.; Barreiros, S.; Brunner, G. Biocatalytic separation of (*R,S*) - 1-phenylethanol enantiomers and fractionation of reaction products with supercritical carbon dioxide. *J. Supercrit. Fluids* **2011**, *55*, 963−970.

(17) Serbanovic, A.; Branco, L. C.; Nunes da Ponte, M.; Afonso, C. A. M. Osmium catalyzed asymmetric dihydroxylation of methyl trans-cinnamate in ionic liquids, followed by supercritical CO_2 product recovery. *J. Organomet. Chem.* **2005**, *690*, 3600−3608.

(18) Harwardt, T.; Francio, G.; Leitner, W. Continuous-flow homogeneous catalysis using the temperature-controlled solvent properties of supercritical carbon dioxide. *Chem. Commun.* **2010**, *46*, 6669−6671.

(19) Peng, D.; Robinson, D. B. New 2-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(20) Mathias, P. M.; Klotz, H. C.; Prausnitz, J. M. Equation-of-state mixing rules for multicomponent mixtures − the problem of invariance. *Fluid Phase Equilib.* **1991**, *67*, 31−44.

(21) Pfohl, O.; Petkov, S.; Brunner, G. *Usage of PE - A Program to Calculate Phase Equilibria*; Herbert Utz Verlag: München, 1998.

(22) Podila, S.; Plasseraud, L.; Cattey, H.; Ballivet-Tkatchenko, D.; Carrera, G. V. S. M.; Nunes da Ponte, M.; Neuberg, S.; Behr, A. Synthesis of 1,2-glycerol carbonate from carbon dioxide: The role of methanol in fluid phase equilibrium. *Indian J. Chem. Sect. A* **2012**, *51*, 1330−1338.

(23) Span, R.; Wagner, W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 110 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509−1596.

(24) Adrian, T.; Maurer, G. Solubility of Carbon Dioxide in Acetone and Propionic Acid at Temperatures between 298 and 333 K. *J. Chem. Eng. Data* **1997**, *42*, 668−672.

(25) Hongling, L.; Rongjiao, Z.; Wei, X.; Hongfei, X.; Zeliang, D.; Yiling, T. Vapor-Liquid Equilibrium Data of (Carbon Dioxide + Methyl Propionate) and (Carbon Dioxide + Propyl Propionate) at Pressures from (1.00 to 12.00) MPa and Temperatures from (313.0 to 373.0) K. *J. Chem. Eng. Data* **2009**, *54*, 1510−1517.

(26) Yaws, C. L. *Thermophysical Properties of Chemicals and Hydrocarbons*, 1st ed.; William Andrew Inc.: New York, 2008.

DOI: 10.1021/acs.jced.6b00595
J. Chem. Eng. Data XXXX, XXX, XXX−XXX