Journal of chemical & engineering data

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pubs.acs.org/jced

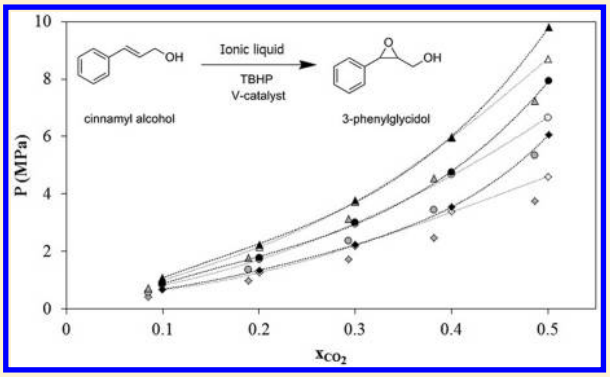
Effect of Carbon Dioxide Addition on the Phase Behavior of Epoxidation Reaction Mixtures in Ionic Liquids

Somayeh Kazemi,[†] Cor J. Peters,[†,‡] and Maaike C. Kroon*,[†]

[†]Department of Chemical Engineering and Chemistry, Separation Technology Group, Eindhoven University of Technology, Den Dolech 2, 5612 AZ Eindhoven, Netherlands

[‡]Chemical Engineering Program, The Petroleum Institute, P.O. Box 2533, Abu Dhabi, United Arab Emirates

ABSTRACT: Volatile organic compounds can be replaced by more benign alternatives, such as ionic liquids (ILs) and supercritical carbon dioxide ($scCO_2$). Previously, we showed that ILs offer advantages as solvents for epoxidation reactions (Kazemi et al. *Green Process Synth.*, **2012**, *1*, 509−516). In this study, the high-pressure phase behavior of ternary systems containing the epoxidation reaction compounds with ILs and CO_2 is measured in order to design the reaction and subsequent separation step. The organic compounds studied are cinnamyl alcohol (reactant) and (2*S*,3*S*)-(−)-3-phenylglycidol (product), and the IL used is 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim]-[Tf_2N]). Phase behavior experiments are carried out using a synthetic method in the Cailletet apparatus at five different concentrations of CO_2 and temperatures and pressures up to 368 K and 12.1 MPa, respectively. Both ternary systems only show one type of phase transition. A comparison between the two systems shows that both systems behave similarly at low pressures, while the solubility of CO_2 in the ternary system containing cinnamyl alcohol becomes lower at high pressures. Moreover, a comparison between the binary system of [bmim][Tf_2N] + CO_2 and the studied ternary systems is made. Finally, using data obtained during this work, the conditions for carrying out the epoxidation reaction in a homogeneous phase and extracting the product with supercritical CO_2 in the two-phase region are determined.



1. INTRODUCTION

Epoxides are versatile intermediates, which can be modified to produce a range of important building blocks. They are produced via epoxidation reactions.[1−3] Traditionally, epoxidation reactions are performed in the presence of volatile organic solvents. There is an increasing pressure to replace these volatile organic compounds with more green and environmentally benign solvents. During the past decades, ionic liquids (ILs) and supercritical carbon dioxide ($scCO_2$) have been studied as alternative solvents for chemical reactions and separations.[4−6]

Owing to their unique properties, ILs have attracted a lot of attention as "potential green" solvents to replace conventional organic solvents. ILs are molten salts, which are liquid below 100 °C. They consist of organic cations with organic or inorganic anions. Typically, ILs possess a negligible vapor pressure, a high thermal stability, and a wide liquid range.[7] ILs show high solubility for both polar and apolar compounds. As a result of these properties, there are many reports where ILs have been used as solvents for chemical reactions.[5,8−10]

Previously, we have studied the epoxidation reaction of cinnamyl alcohol to 3-phenylglycidol (Figure 1) in the presence of ILs as solvents.[11] (2*S*,3*S*)-(−)-3-Phenylglycidol is an intermediate for a well-known potent active anti-inflammatory agent, ibuprofen.[12,13] The catalytic epoxidation reaction of cinnamyl alcohol in the presence of ILs has been optimized with respect to variable parameters: (i) type and amount of oxidizing agent, (ii) type and amount of catalyst, (iii) type of IL, and (iv) temperature.[11] Optimum conditions were obtained using the IL 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) with 3 mol % vanadyl acetylacetonate as a catalyst and 1.5 equiv of *tert*-butyl hydroperoxide as oxidant at 25 °C. One of the main advantages of using ILs as solvent for this epoxidation reaction was the higher stability of the epoxides in ILs compared to that in conventional organic solvents.

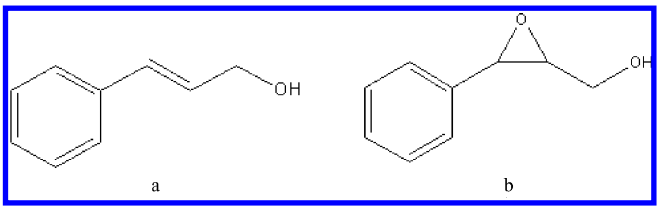


Figure 1. Molecular structure of studied chemical compounds: (a) cinnamyl alcohol, (b) (2*S*,3*S*)-(−)-3-phenylglycidol.

Received: December 10, 2012
Accepted: April 23, 2013

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Owing to the extremely low vapor pressure of ILs, low-temperature distillation can be regarded as an option for product recovery. However, it is not suitable for thermally unstable products like (2*S*,3*S*)-(−)-3-phenylglycidol.[14] Another alternative is to use supercritical CO_2 to extract the products from ILs, because ILs do not dissolve in CO_2, but CO_2 is highly soluble in ILs.[15,16] Moreover, it was shown before that CO_2 is able to force two immiscible liquid phases to form one homogeneous phase at CO_2 pressure increase.[17,18] This interesting behavior of CO_2, which is known as the miscibility switch phenomenon, is generally applicable for ternary systems containing ILs, CO_2, and organics.[19] A new process setup based on this phase behavior has been proposed.[20] In this process setup, the reaction can be carried out in a homogeneous phase at a high rate (no mass transfer limitations)[21] by selection of a suitable pressure, temperature, and CO_2 concentration. After completion of the reaction, a phase split is induced by changing the conditions. The product can be recovered with high purity from one of the two phases that is substantially free of IL.

To apply this new process setup it is important to detect the homogeneous and heterogeneous phase conditions. Therefore, it is crucial to have knowledge on the phase behavior of the ternary systems containing ILs, CO_2, and the organic reactant/product of the chemical reactions. There are already various studies on the phase behavior of ternary IL + CO_2 + organic solute systems available.[15,19,22−29] These studies showed that the location of the phase transitions is greatly affected by the type of the organic, the type of the IL, and their concentrations in the system.[22,26,27,30] It was also shown that CO_2 at low concentrations acts as a cosolvent by increasing the solubility of organics into the IL phase, whereas CO_2 at higher concentrations acts as an antisolvent by decreasing the solubility of organics in the IL phase.[27,29,31]

In this contribution, we will further investigate the phase behavior of the ternary systems containing CO_2, the IL [bmim][Tf_2N] and an organic compound from the epoxidation reaction mixture, for example, cinnamyl alcohol (reactant) or (2*S*,3*S*)-(−)-3-phenylglycidol (product). Phase behavior experiments are carried out in the Cailletet apparatus using a synthetic method in the temperature range from 278 K to 368 K and pressures up to 12.1 MPa. The CO_2 concentration is varied from 10 % mol to 50 % mol. The conditions at which the different phase transitions occur are measured.

2. EXPERIMENTAL SECTION

Materials. The IL 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) (99 %) was purchased from Iolitec. The IL was dried prior to use and the water content was measured by Karl Fischer analysis to be less than 0.01 %. Cinnamyl alcohol (98 %) was supplied from Aldrich and (2*S*,3*S*)-(−)-3-phenylglycidol (99 %) was purchased from Fluka. Both chemicals were used as received. High purity CO_2 (99.99 %) was purchased from HoekLoos B.V.

Methodology. Phase behavior measurements were carried out according to the synthetic method using the Cailletet apparatus. The main part of the Cailletet apparatus is a thick-walled Pyrex glass tube, also known as the Cailletet tube, where the samples with known overall composition were placed. The Cailletet tube was closed at one end and open at the other end. From the open end necessary pressure was transmitted to the samples through the mercury column. Prior to phase behavior measurements, a solution of 20 mol % of cinnamyl alcohol (or (2*S*,3*S*)-(−)-3-phenylglycidol) in [bmim][Tf_2N] was prepared to keep the concentration of the solution constant during all the experiments. Then, this solution was injected into the Cailletet tube using a microsyringe. The sample was degassed using a vacuum pump, while the sample remained frozen using liquid nitrogen in order to prevent the loss of the sample. After degassing this solution, the desired amount of CO_2 was injected volumetrically to the Cailletet tube using the gas-rack system. Finally, the Cailletet tube, which contained the solute + IL + CO_2 and was sealed with mercury, was mounted into the Cailletet apparatus.

In general, temperature was kept constant in the sample and pressure was varied until the phase transition was observed visually. In this case, bubble points were measured when the last bubble of the gas disappeared in the sample. A schematic representation of the setup is shown in Figure 2, and more detailed information of the set up and procedures can be found elsewhere.[32] The experiments were performed in a temperature range from 278 K to 368 K and pressures up to 12.1 MPa were applied. The accuracy of the measurements for the temperature was ± 0.01 K and for the pressure this was ± 0.003 MPa.

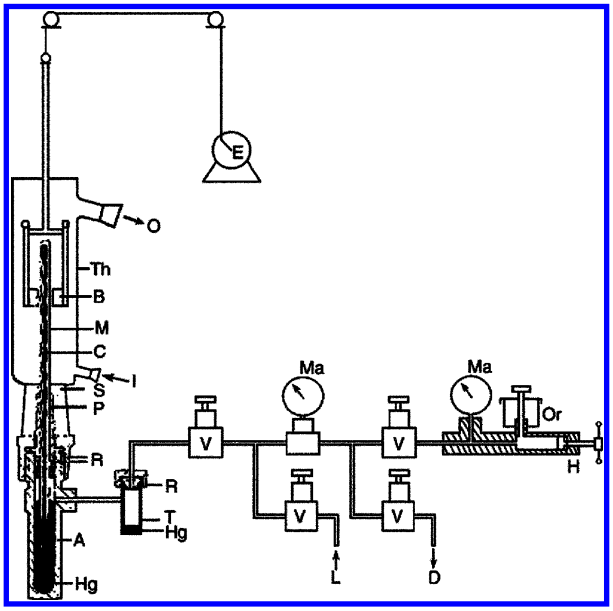

Figure 2. The Cailletet apparatus: A, autoclave; B, magnets; C, capillary glass tube; D, drain; E, motor; H, rotating hand pump; Hg, mercury; I, thermostat liquid in; L, line to dead weight pressure gauge; M, mixture being investigated; Ma, manometers; O, thermostat liquid out; Or, hydraulic oil reservoir; P, closing plug; R, Viton O-rings; S, silicone rubber stopper; T, mercury trap; Th, glass thermostat; V, valve.[32]

3. RESULTS AND DISCUSSION

Experimental bubble point data for the ternary systems of cinnamyl alcohol + [bmim][Tf_2N] + CO_2 and (2*S*,3*S*)-(−)-3-phenylglycidol + [bmim][Tf_2N] + CO_2 are presented in Tables 1 and 2, respectively. The data were measured within a temperature range of 278 K to 368 K and pressures up to 12.1 MPa were applied. In total, five different concentrations of CO_2 (from 10 mol % to 50 mol %) were investigated. For all systems studied, the ratio of the concentration of solutes (cinnamyl alcohol and (2*S*,3*S*)-(−)-3-phenylglycidol) to the IL [bmim]-[Tf_2N] was kept constant at 20.0 mol %. Data from Tables 1

Table 1. Experimental Bubble Point Data for Different Molar Fractions of CO_2 (x_{CO_2}) in the System Cinnamyl Alcohol + [bmim][Tf_2N] + CO_2 (20.00 mol % Solute with Respect to IL)[a]

x_{CO_2}	T/ K	P/ MPa	T/ K	P/ MPa	T/ K	P/ MPa
0.0995	278.40	0.406	313.46	0.676	348.46	1.046
	283.43	0.426	318.42	0.728	353.44	1.107
	288.32	0.461	323.40	0.793	358.39	1.187
	293.36	0.511	328.48	0.828	363.49	1.252
	298.43	0.551	333.41	0.893	368.50	1.303
	303.36	0.586	338.51	0.936		
	308.45	0.646	343.45	0.986		
0.2001	278.46	0.677	313.36	1.302	348.32	2.148
	283.40	0.762	318.38	1.412	353.36	2.278
	288.40	0.832	323.40	1.522	358.45	2.413
	293.39	0.912	328.40	1.618	363.45	2.553
	298.40	1.012	333.39	1.763	368.49	2.699
	303.35	1.077	338.39	1.888		
	308.32	1.202	343.32	2.008		
0.3000	278.40	1.052	313.43	2.153	348.49	3.655
	283.32	1.252	318.41	2.328	353.50	3.805
	288.43	1.327	323.39	2.543	358.50	4.095
	293.42	1.502	328.44	2.718	363.48	4.330
	298.42	1.627	333.46	2.969	368.42	4.505
	303.35	1.778	338.46	3.144		
	308.39	2.028	343.48	3.405		
0.3996	278.43	1.776	313.39	3.395	348.37	5.681
	283.32	1.953	318.38	3.707	353.40	6.076
	288.39	2.176	323.31	3.978	358.50	6.471
	293.43	2.368	328.33	4.298	363.51	6.965
	298.46	2.596	333.42	4.619	368.75	7.261
	303.35	2.818	338.38	4.965		
	308.42	3.114	343.41	5.336		
0.5009	278.40	3.240	313.37	5.871	348.42	9.434
	283.39	3.590	318.38	6.232	353.34	10.034
	288.38	3.956	323.39	6.782	358.42	10.610
	293.39	4.331	328.43	7.217	363.48	11.251
	298.29	4.607	333.32	7.778	368.47	12.100
	303.40	4.982	338.39	8.383		
	308.34	5.432	343.40	8.884		

[a]Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.003 MPa, and $u(x_{CO_2})$ = 0.005.

Table 2. Experimental Bubble Point Data for Different Molar Fractions of CO_2 (x_{CO_2}) in the System (2S,3S)-(−)-3-phenylglycidol + [bmim][Tf_2N] + CO_2 (20.00 mol % Solute with Respect to IL)[a]

x_{CO_2}	T/ K	P/ MPa	T/ K	P/ MPa	T/ K	P/ MPa
0.0998	278.32	0.432	313.39	0.652	348.39	0.963
	283.29	0.457	318.36	0.697	353.40	1.013
	288.35	0.482	323.36	0.742	358.43	1.063
	293.40	0.517	328.41	0.773	363.39	1.103
	298.35	0.562	333.40	0.818	368.48	1.143
	303.36	0.597	338.40	0.853		
	308.40	0.622	343.40	0.903		
0.2003	278.29	0.599	313.41	1.239	348.43	2.051
	283.37	0.669	318.35	1.349	353.47	2.192
	288.35	0.744	323.45	1.449	358.49	2.322
	293.37	0.839	328.46	1.565	363.51	2.442
	298.36	0.939	333.43	1.690	368.38	2.552
	303.38	1.049	338.39	1.805		
	308.35	1.129	343.45	1.910		
0.3000	278.30	1.012	313.40	2.093	348.46	3.495
	283.36	1.143	318.40	2.273	353.44	3.775
	288.38	1.273	323.43	2.453	358.46	4.015
	293.34	1.418	328.46	2.653	363.50	4.276
	298.29	1.573	333.42	2.853	368.48	4.415
	303.40	1.743	338.38	3.094		
	308.41	1.914	343.41	3.315		
0.4003	278.29	1.454	313.36	3.215	348.34	5.655
	283.35	1.674	318.39	3.554	353.44	6.055
	288.34	1.894	323.37	3.893	358.40	6.435
	293.38	2.134	328.37	4.193	363.43	6.817
	298.36	2.375	333.40	4.514	368.42	7.217
	303.34	2.633	338.38	4.894		
	308.27	2.894	343.43	5.274		
0.4998	278.34	2.215	313.49	4.718	348.34	8.212
	283.28	2.495	318.40	5.138	353.46	8.793
	288.30	2.786	323.37	5.619	358.40	9.454
	293.40	3.096	328.32	6.119	363.42	10.074
	298.36	3.436	333.33	6.619	368.35	10.675
	303.31	3.818	338.41	7.071		
	308.31	4.258	343.39	7.632		

[a]Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.003 MPa, and $u(x_{CO_2})$ = 0.005.

and 2 are plotted in pressure versus temperature graphs in Figures 3 and 4, respectively. From these figures it can be noticed that the two systems show only liquid−vapor to liquid transitions within the conditions studied. This is contrary to what has been observed in other ternary IL + CO_2 + organic systems, in which also liquid−liquid, solid−liquid, and three-phase regions have been identified.[25,27] Moreover, it can be observed that increasing the temperature has a reverse effect on the CO_2 solubility in both systems. In other words, by increasing the temperature, higher pressures are necessary to dissolve the CO_2 in the ternary systems. An increase in CO_2 concentration results in an increase in pressure in order to reach a homogeneous liquid phase.

This can be better observed from Figure 5, where the pressure is plotted against the concentration of CO_2. A third-order polynomial fit of the data from Tables 1 and 2 is used to obtain the lines (isotherms) in Figure 5. In this figure also, the bubble point data of the binary IL + CO_2 system are added as points for comparison.[33] It can be observed that both organic compounds (cinnamyl alcohol and (2S,3S)-(−)-3-phenylglycidol) decrease the solubility of CO_2 in the liquid phase, because higher pressures are needed to completely dissolve the same amount of CO_2. This behavior can be explained on the basis of CO_2−IL interactions. Previously, it was found that the solubility of CO_2 in an IL is mainly caused by the strong interactions between the CO_2 molecules and the anions of ILs.[34−36] Because cinnamyl alcohol (or 3-phenylglydicol) competes with CO_2 in the ternary system for these interaction sites, the solubility of the CO_2 is lower in the ternary systems compared to the binary system. Moreover, this could be due to a dilution effect which is caused by addition of organics.

From Figure 5 it can also be seen that both ternary systems show similar phase behavior at concentrations of CO_2 up to 40 mol %. This behavior can be explained by the similarity of the molecular structure of the two components as shown in Figure 1. However, by further increasing the concentration of CO_2, the difference in the phase behavior of these two systems is more pronounced. At CO_2 concentrations higher than 40 mol %,

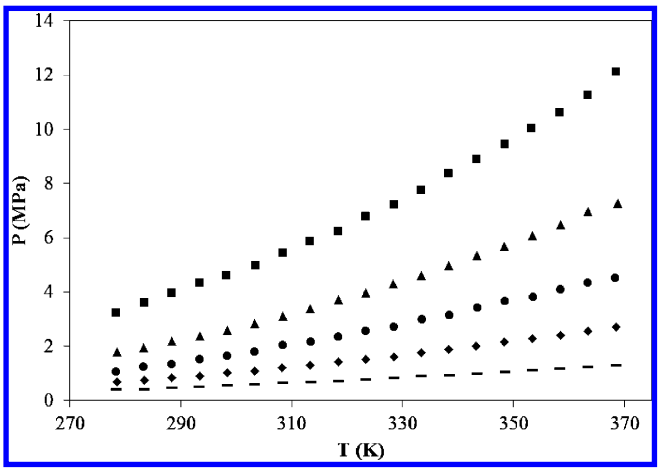

Figure 3. Experimental bubble point data (LV → L) for the ternary system of cinnamyl alcohol + [bmim][Tf_2N] + CO_2, at different concentrations of CO_2: solid bar, 9.95 mol % CO_2; ♦, 20.01 mol % CO_2; ●, 30.00 mol % CO_2; ▲, 39.96 mol % CO_2; ■, 50.09 mol % CO_2.

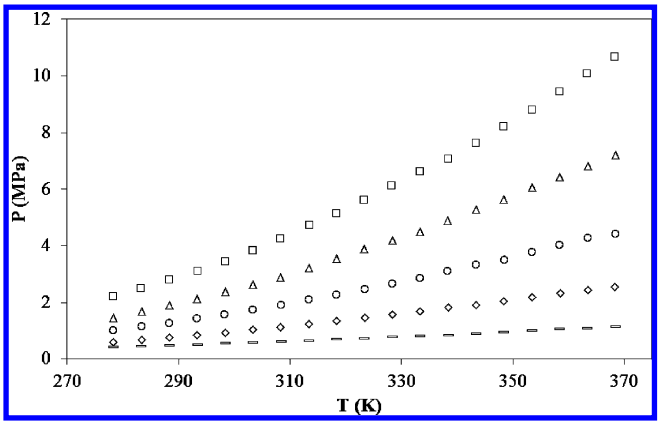

Figure 4. Experimental bubble point data (LV → L) for the ternary system of (2S,3S)-(-)-3-phenylglycidol + [bmim][Tf_2N] + CO_2, at different concentrations of CO_2: open bar, 9.98 mol % CO_2; ◇, 20.03 mol % CO_2; ○, 30.00 mol % CO_2; Δ, 40.03 mol % CO_2; □, 49.98 mol % CO_2.

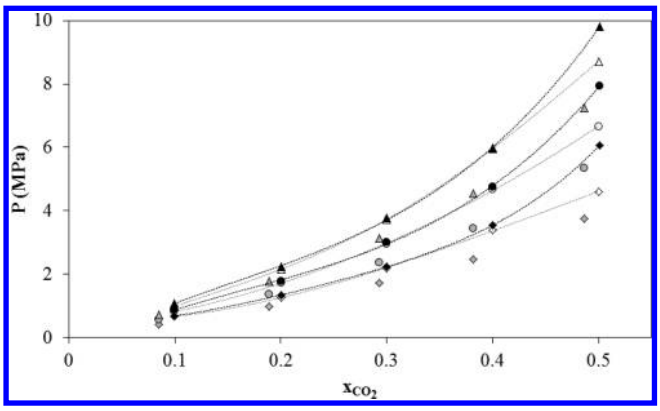

Figure 5. Comparison between isotherms for the binary system [bmim][Tf_2N] + CO_2 (gray symbols), ternary systems of cinnamyl alcohol + [bmim][Tf_2N] + CO_2 (filled symbols connected with lines), and (2S,3S)-(−)-3-phenylglycidol + [bmim][Tf_2N] + CO_2 (open symbols connected with lines) at different temperatures: ◇, 313,15 K; ○, 333,15 K; Δ, 353,15 K.

higher pressures are necessary to completely dissolve CO_2 in the system containing cinnamyl alcohol compared to (2S,3S)-(−)-3-phenylglycidol. One possible reason is that (2S,3S)-(−)-3-phenylglycidol is more bulky, so that it can facilitate the uptake of larger amounts of CO_2. We have also checked the possibility of a chemical reaction occurring between the epoxide ring and the CO_2. For this purpose, the ternary system of (2S,3S)-(−)-3-phenylglycidol + IL + CO_2 was left under pressure for 24 h. After analyzing the samples from this solution, there was no indication of a chemical reaction.

Finally, it can be concluded from the experimental data that a homogeneous phase can be reached in these systems, so that it is possible to use the miscibility switch phenomenon to carry out epoxidation reactions in IL + CO_2 mixtures. For instance, at CO_2 concentrations of 40 mol %, a homogeneous phase can be reached at 298 K and pressures higher than 4 MPa. The temperature (298 K) is the optimum reaction temperature which was found before during kinetic studies.[11] To extract the product using CO_2, it is necessary to induce the two-phase region in the system and CO_2 is either in the liquid or the supercritical state. Therefore, for product recovery using supercritical CO_2 temperatures at 333 K and pressures lower than 8 MPa should be applied.

4. CONCLUSIONS

In this work, the phase behavior of two ternary systems, that is, [bmim][Tf_2N] + CO_2 + cinnamyl alcohol and [bmim][Tf_2N] + CO_2 + (2S,3S)-(−)-3-phenylglycidol, has been measured. For both systems, only liquid−vapor to liquid transitions have been detected within the operational conditions of our experiments. It is shown that higher pressures are necessary to reach a homogeneous phase when increasing the temperature and the concentration of CO_2. At lower concentrations of CO_2 (below 40 mol %), both ternary systems have similar phase behavior due to the similarity in molecular shape of the organics. However, at higher CO_2 concentrations (above 40 mol %), higher pressures are required to completely dissolve CO_2 in the ternary system containing cinnamyl alcohol. A comparison between the binary system of [bmim][Tf_2N] + CO_2 and the studied ternary systems indicates that the addition of organic compounds decreases the solubility of CO_2 in [bmim][Tf_2N]. Finally, conditions for carrying out the reaction in a homogeneous region (T = 298 K, p > 4 MPa, x_{CO_2} = 40 mol %) and the separation in a heterogeneous region (T = 333 K, p < 8 MPa) are determined.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: m.c.kroon@tue.nl. Tel.: +31-40-2475289. Fax: +31-40-2463966.

Funding

Financial support by Agentschap NL is also gratefully acknowledged.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank Eugene Straver for technical support.

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