

Research Article

Phase Behavior at High Pressure of the Ternary System: CO₂, Ionic Liquid and Disperse Dye

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High pressure phase behavior experimental data have been measured for the systems carbon dioxide (CO₂) + 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim] [PF₆]) and carbon dioxide (CO₂) + 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim] [PF₆]) + 1-amino-2-phenoxy-4-hydroxyanthraquinone (C.I. Disperse Red 60). Measurements were performed in the pressure up to 18 MPa and at the temperature (323 to 353 K). As reported in the literature, at higher concentrations of carbon dioxide the phase transition pressure increased very steeply. The experimental data for the binary and ternary systems were correlated with good agreement using the Peng-Robinson equation of state. The amount of water in phase behavior of the systems was evaluated.

1. Introduction

In the past years the development of new technologies to minimize water consumption and wastewater emissions received more attention. In this context, the textile industry has a significant stake in the generation of effluents with highly pollution potential, using large amounts of water with chemical additives [1]. The process of dyeing using supercritical fluids is an alternative method that does not use water and any additive is frequently not required. In addition, such process allows the recovering and the reusing of the dyes. According to van der Kraan et al. [2], in dyeing of textiles consisting of nonpolar materials such as polyester, supercritical CO₂ acts as a blowing agent and increases the rate of diffusion of the dye molecules inside the fiber. Several studies have been reported on this textile-dyeing technology [3–6]. The literature describes applications of supercritical technology in combination with the ionic liquids in both the extraction and the separation processes and as an alternative solvent for organic and inorganic compounds in reaction

mediums [7–9]. The ionic liquids are described as “designer solvents,” where their characteristics can be adjusted to make the change either of cations or anions, or both. In this way, dyeing process involving association of supercritical technology with ionic liquids (ILs) can be used to improve the solubility of the dyes in the dyeing process of textile fibers and minimize the amount of energy demand.

In this context, the objective of this work is to report new experimental data of CO₂ (1) + 1-butyl-3-methylimidazolium hexafluorophosphate [bmim] [PF₆] + (2) and CO₂ (1) + [bmim] [PF₆] (2) C.I. Disperse Red 60 systems in the temperature range of 323 to 353 K. C.I. Disperse Red 60 is indeed a popular dye and one of the widely used dyes in dyeing process of synthetic textile fibers [2, 10, 11]. [bmim] [PF₆] is one of the most studied ionic liquids (ILs) in the literature with great availability of physical and chemical data as well as phase equilibrium data [12–14]. Keskin et al. [7], Huddleston et al. [15], and Jaitely et al. [16] have reported that the ionic liquid consisting of imidazole as a cation and [PF₆]⁻ as an anion presents hydrophobic characteristics

TABLE 1: Experimental data of (L → LV) of binary system CO₂ (1) + [bmim] [PF₆] (2).

X_1	Temperature [K]	Pressure [MPa]	% Water _{after}	% Water _{before}
30.0×10^{-2}	333 ± 0.1	4.53 ± 0.1	0.085 ± 0.02	0.26 ± 0.02
40.0×10^{-2}	333 ± 0.1	6.64 ± 0.1	0.085 ± 0.02	0.26 ± 0.02
47.0×10^{-2}	333 ± 0.1	8.06 ± 0.4	0.085 ± 0.02	0.26 ± 0.02
50.0×10^{-2}	333 ± 0.1	9.83 ± 0.3	0.085 ± 0.02	0.26 ± 0.02

compatible to that of disperse dyes with wide uses in dyeing of synthetic fibers. The synthetic static method with variable-volume cell was used in the experimental measurements of phase equilibrium. The amount of water present in ILs was determined by Karl Fischer analysis before and after equilibrium measures once that the ionic liquid [bmim] [PF₆] absorbs the moisture during the synthesis process due to its hygroscopic property [17]. A small amount of water in the ionic liquid can have a dramatic effect on the phase equilibrium behavior [13]. A technique to recover [bmim] [PF₆] from the [bmim] [PF₆] + C.I. Disperse Red 60 mixture was also proposed here once the reuse of [bmim] [PF₆] makes the dyeing process more environmentally benign and economically attractive. Peng-Robinson equation of state with quadratic mixing rules was used to correlate the experimental data.

2. Experimental

2.1. Materials. Commercial CO₂ and nitrogen (99%) were purchased from White Martins (Rio de Janeiro, Brazil). 1-Methylimidazole (99.0% GC) and 1-Bromobutane (96.0% GC) were purchased from Fluka (Sigma-Aldrich Ltda, Brazil). Ethyl acetate (99.5% P.A.), acetone (99.5% P.A.), activated charcoal (P.A.), anhydrous methanol (99.8% HPLC), dichloromethane (99.5% P.A.), and ethyl ether were purchased from Nuclear (CAQ-Chemical of Home Ind. Com. Ltda, Brazil). Potassium hexafluorophosphate (98% GC) was obtained from Aldrich (Sigma-Aldrich Ltda, Brazil). Silica gel mesh 0.035–0.070, 60 Å 99.5% was obtained from Acros (Sigma-Aldrich Ltda, Brazil). The Karl Fisher reagent (99.99% HPLC) was purchased from Merck (Merck S.A-Brazil). All water concentrations were measured through Karl Fischer (Analyzer, KF-1000) analysis. The 1-amino-2-phenoxy-4-hydroxyanthraquinone (disperse Red 60) was supplied by DyStar (Brazil).

The ionic liquid [bmim] [PF₆] was synthesized from 1-methylimidazol, bromobutane and potassium hexafluorophosphate (KPF₆) by the process described in the literature [18]. [bmim] [PF₆] was dried under vacuum at 333 K and stored under dried nitrogen. It was purified in a chromatography column with silica gel Acros (Sigma-Aldrich Ltda, Brazil). (silica gel 60; mesh 70–230) and dichloromethane. Hydrogen and Carbon Nuclear Magnetic Resonance (¹H and ¹³C NMR) analyses of the [bmim] [PF₆] obtained were δH (300 MHz; CDCl₃) 8.34 (sl, 3 N–CH₃–N), 7.31 (*t*, CH₂=CH), 7.28 (*t*, CH=CH₂), 4.09 (*t*, N–CH₂), 3.83 (*s*, N–CH₃), 1.78 (quintet, CH₂–CH₂), 1.27 (sextet, CH₂–CH₃),

0.85 (*t*, CH₂–CH₃) for δC (75 MHz, CDCl₃) 135.8 (N–CH₂–N), 123.8 (CH₂=CH), 122.5 (CH=CH₂), 49.8 (N–CH₂), 36.1 (N–CH₃), 31.8 (CH₂–CH₂), 19.3 (CH₂–CH₃), 13.3 (CH₂–CH₃). The analyses using NMR were performed in a Varian spectrometer, model Mercury Plus BB using CDCl₃ as a solvent.

2.2. Equipment and Procedure. Phase equilibrium experiments (cloud points) were performed through the synthetic static method [19] in a high-pressure variable-volume view cell. The experimental apparatus and experimental procedure are similar to those used in previous studies of phase equilibrium carried out by our group [20–22]. Briefly, the experiment begins with the introduction of a predetermined amount of compounds (CO₂, IL, and dye) in the equilibrium cell so that the global composition of the mixture is known. In the sequence, the system was stirred for 12 h at room temperature for complete solubilization of CO₂ in [bmim] [PF₆]. The procedure used here follows the work of Aki et al. [23]. After the initial procedure, pressure and temperature are adjusted to form a homogeneous solution. After reaching the thermal equilibrium of the system, pressure is slowly decreased until the appearance of a second phase is visually detected.

After the measurements of the phase transitions, the IL + Dye mixture was submitted to a process to recover the IL. The process of IL recovery consisted of the addition of a dichloromethane solution and active coal in the mass ration of 1:3 into the mixture of IL + Dye. Afterwards, the solution was stirred at room temperature for 48 h. Then, the mixture was filtrated using qualitative filter paper in a chromatographic column with silica gel (silica gel 60 Å; mesh 0.035–0.70 mm). The purified solution was evaporated under vacuum at 343 K for 10 h.

The values of water content refer to values obtained before and after the phase equilibrium measurements. For the binary system CO₂ + [bmim] [PF₆] the water content was $0.10 \pm 0.02\%$ (after phase equilibrium) and 0.23 ± 0.02 (before measurement). For the ternary system CO₂ + [bmim] [PF₆] + C.I. disperse Red 60 the water content corresponded to 0.43 ± 0.04 and 0.26 ± 0.02 , after and before measurements, respectively. For the binary system with IL recovered the measurement were 0.19 ± 0.01 and 0.66 ± 0.02 , after and before, respectively.

2.3. Thermodynamic Modeling. Peng-Robinson equation [24] of state was used to model the vapor-liquid equilibrium data:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)}. \quad (1)$$

The parameters *a* and *b* were calculated through the following mixing rules:

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} y_i y_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (2)$$

$$b = \sum_{j=1}^{nc} y_j b_j,$$

TABLE 2: Experimental data of liquid-vapor ternary system CO₂ (1) + [bmim] [PF₆] (2) + Red Dye 60 (3).

X_1	X_2	X_3	Temperature [K]	Pressure [MPa]	% Water _{after}	% Water _{before}
30.0×10^{-2}	69.9×10^{-2}	0.1×10^{-2}	323 ± 0.1	4.41 ± 0.2	0.32 ± 0.01	0.83 ± 0.02
			333 ± 0.1	5.05 ± 0.1	0.32 ± 0.01	0.83 ± 0.02
			343 ± 0.1	5.69 ± 0.1	0.32 ± 0.01	0.83 ± 0.02
			353 ± 0.1	6.38 ± 0.1	0.32 ± 0.01	0.83 ± 0.02
33.0×10^{-2}	66.9×10^{-2}	0.1×10^{-2}	323 ± 0.1	5.41 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			333 ± 0.1	6.05 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			343 ± 0.1	6.76 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			353 ± 0.1	7.44 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
35.0×10^{-2}	64.9×10^{-2}	0.1×10^{-2}	323 ± 0.1	5.84 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			333 ± 0.1	6.91 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			343 ± 0.1	8.10 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			353 ± 0.1	9.39 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
40.0×10^{-2}	59.9×10^{-2}	0.1×10^{-2}	323 ± 0.1	6.25 ± 0.1	0.32 ± 0.01	0.83 ± 0.02
			333 ± 0.1	7.21 ± 0.1	0.32 ± 0.01	0.83 ± 0.02
			343 ± 0.1	8.25 ± 0.1	0.32 ± 0.01	0.83 ± 0.02
			353 ± 0.1	9.37 ± 0.1	0.32 ± 0.01	0.83 ± 0.02
43.0×10^{-2}	56.9×10^{-2}	0.1×10^{-2}	323 ± 0.1	7.05 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			333 ± 0.1	8.45 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			343 ± 0.1	10.01 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			353 ± 0.1	11.62 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
46.0×10^{-2}	53.9×10^{-2}	0.1×10^{-2}	323 ± 0.1	8.15 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			333 ± 0.1	9.31 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			343 ± 0.1	10.54 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			353 ± 0.1	11.99 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
50.0×10^{-2}	49.9×10^{-2}	0.1×10^{-2}	323 ± 0.1	8.42 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			333 ± 0.1	10.28 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			343 ± 0.1	12.41 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
			353 ± 0.1	14.72 ± 0.1	0.14 ± 0.03	0.24 ± 0.05
53.0×10^{-2}	46.9×10^{-2}	0.1×10^{-2}	323 ± 0.1	10.87 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			333 ± 0.1	13.01 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			343 ± 0.1	15.26 ± 0.1	0.25 ± 0.02	0.34 ± 0.04
			353 ± 0.1	17.68 ± 0.1	0.25 ± 0.02	0.34 ± 0.04

where y_i is the molar fraction of the component i and a_i and b_i are the Peng-Robinson parameters for the pure component i . The binary interaction parameters, k_{ij} , were determined through the correlation of experimental data obtained in this work. The optimization procedure employed for fitting k_{ij} was based on the Nelder and Mead simplex method [25].

3. Results and Discussion

Experimental data of phase transitions at high pressures of the CO₂ (1) + [bmim] [PF₆] (2) binary system at 333 K are presented in Figure 1 and Table 1. All phase transitions observed were vapor-liquid type. The CO₂ (1) solubility in [bmim] [PF₆] (2) presented in Figure 1 is compared with experimental data reported by Blanchard and Brennecke [26] and Fu et al. [17]. Solubility obtained here is in agreement with Fu et al. [17] data. However, experimental

data reported by Blanchard and Brennecke [26] show a significant divergence compared to the results obtained in this work. Fu et al. [17] state that the discrepancy in the solubility measurements can be attributed to different experimental techniques, uncertainties in the experimental procedure, impurity in the IL, among other factors. From our own point of view, the differences verified in this figure are mainly due to the water content in the ionic liquids used in the experiments. Blanchard and Brennecke [26] reported 0.15% water content in IL prior to experimental measures. However, water content data after the experiments have not yet been reported.

It is possible to notice that CO₂ solubility in the IL increases continually with pressure, reaching 0.50 at 333 K and 9.83 MPa. Such behavior is also reported by Bermejo et al. [27], Kamps et al. [14], and Shariati and Peters [12].

Figure 2 and Table 2 show the experimental phase behavior for the ternary system CO₂ (1) + [bmim] [PF₆] (2) +

TABLE 3: Experimental data of liquid-vapor binary system carbon dioxide + [bmim] [PF₆]_{recovered}.

X_1	Temperature [K]	Pressure [MPa]	% Water _{after}	% Water _{before}
30.0×10^{-2}	333 ± 0.1	5.70 ± 0.1	0.190 ± 0.010	0.66 ± 0.02
40.0×10^{-2}	333 ± 0.1	7.40 ± 0.1	0.190 ± 0.010	0.66 ± 0.02
45.0×10^{-2}	333 ± 0.1	8.45 ± 0.4	0.190 ± 0.010	0.66 ± 0.02
50.0×10^{-2}	333 ± 0.1	10.61 ± 0.3	0.190 ± 0.010	0.66 ± 0.02

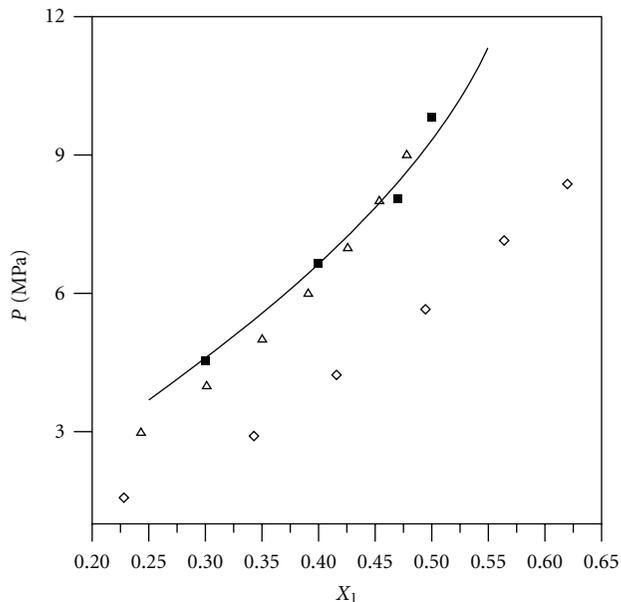


FIGURE 1: Experimental data obtained in this work (■) and reported by Blanchard et al. [13] (◇), Fu et al. [17] (△) for the CO₂(1) + [bmim] [PF₆] (2) binary system at 333 K isotherm. Thermodynamic modeling (—).

TABLE 4: Critical properties and acentric factor of carbon dioxide, ionic liquid and disperse Red 60.

Components	Mw	T_c (K)	P_c (MPa)	ω
CO ₂	44.01	304.2	73.8	0.239
[bmim] [PF ₆]	284.18	708.9	17.3	0.755
Disperse red 60	331.32	1361	30.2	1.370

disperse dye Red 60 (3). In this case, it is possible to notice the increase of CO₂ solubility with increasing pressure, an analogue behavior to that of the binary system. Moreover, CO₂ solubility decreases as temperature increases. The IL addition in supercritical environment induces a significant solubilization of the dispersed dye Red 60, which is almost insoluble in supercritical CO₂ in the temperature and pressure range investigated. The solubility of the dye Red 60 in CO₂ is around 10^{-6} in the investigated range [28]. On the other hand, in this range the solubility of the dye Red 60 in CO₂ and IL has an average value of 10^{-4} . For all experimental conditions (Figures 1 and 2), a good agreement of the Peng-Robinson equation with the experimental data is observed.

Figure 3 shows a comparison of the phase diagram for the systems CO₂ (1) + [bmim] [PF₆] (2) and CO₂ (1) + [bmim]

TABLE 5: PR-EoS binary interaction parameters for the binary and ternary systems.

System	T/K	K_{ij}	AAD%
[bmim] [PF ₆] _{system binary}	333	0.1441	1.34
[bmim] [PF ₆] _{recovered}	333	0.1577	3.45
	323	0.1536	4.65
[bmim] [PF ₆] _{system ternary}	333	0.1616	3.87
	343	0.1709	4.58
	353	0.1787	4.15

[PF₆] (2) + disperse dye Red 60 (3) at 333 K. It is possible to observe that CO₂ shows lower solubility in ionic liquid for the ternary system when compared to the binary system.

Figure 4 shows the phase behavior for the binary systems CO₂ (1) + [bmim] [PF₆] (2) and CO₂ (1) + [bmim] [PF₆]_{recovered} (2). Such results are summarized in Table 3. It can be observed that the phase behavior of both systems (CO₂ (1) + [bmim] [PF₆] (2) and CO₂ (1) + [bmim] [PF₆]_{recovered} (2)) are similar. Solubility differences between these two systems can be attributed to the water content present in each situation. Furthermore, the RMN spectra of IL after removal of the disperse dye Red 60 were consistent with values found for pure LI produced in our laboratory and with those reported in literature [29].

The PR-EoS with the quadratic mixing rules was used to modeling the phase transition experimental data for all systems. The binary interaction parameters in the mixing rules were optimized using the P, x data for each system. The critical properties and acentric factors of the IL were obtained of the Valderrama and Robles [30], and the critical properties, and acentric factors of the disperse dye Red 60 were obtained of the Mishima et al. [31]. The critical properties are presented in Table 4 and Table 5 shows the interaction parameters for each system.

4. Conclusions

It was verified that CO₂ solubility in the ionic liquid decreased by the presence of dye. Such phenomenon results in higher vapor-liquid pressure transitions for the ternary system when compared to the binary system. Water content (impurities) in the systems studied considerably change in the pressure values of phase transition, corroborating literature observations [19, 31, 32]. Therefore, water content in IL synthesis should be carefully controlled. IL's purification protocol for dye removal presented good results without IL physical chemical changes, which enables IL to be reused.

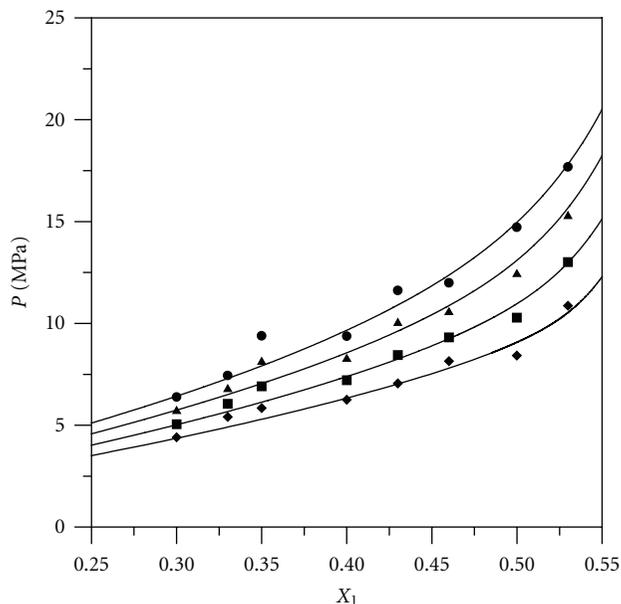


FIGURE 2: Experimental data of bubble-type phase transition at (◆) 323 K, (■) 333 K, (▲) 343 K, and (●) 353 K for the ternary system $\text{CO}_2(1) + [\text{bmim}][\text{PF}_6](2) + \text{disperse dye Red 60}(3)$. Thermodynamic modeling using the Peng-Robinson equation of state (—).

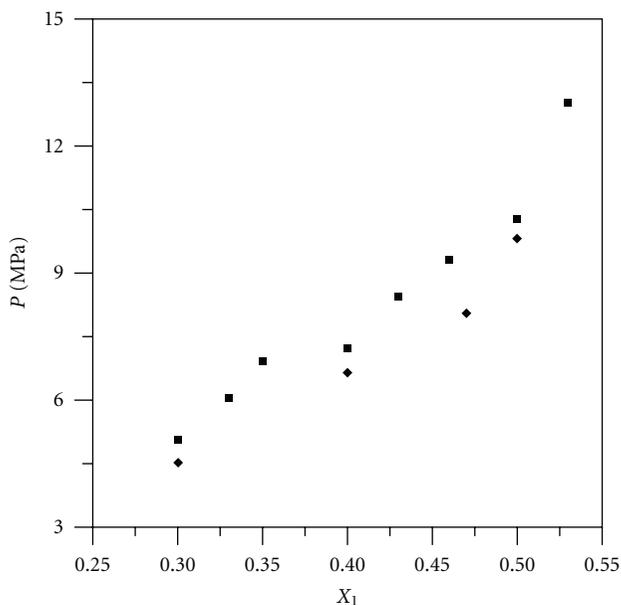


FIGURE 3: Comparison of Px diagram for the binary system $\text{CO}_2(1) + [\text{bmim}][\text{PF}_6](2)$ (◆) and ternary system $\text{CO}_2(1) + [\text{bmim}][\text{PF}_6](2) + \text{disperse dye Red 60}(3)$ (■) at 333 K.

Peng-Robinson equation of state presented a good performance in describing the experimental data observed. The results obtained might be useful in the development of dyeing processes using supercritical fluids in association with ionic liquids. Finally, the results of partition of the undisclosed dye composition between SCCO_2 and an ionic liquid demonstrated that it is possible to increase significantly the

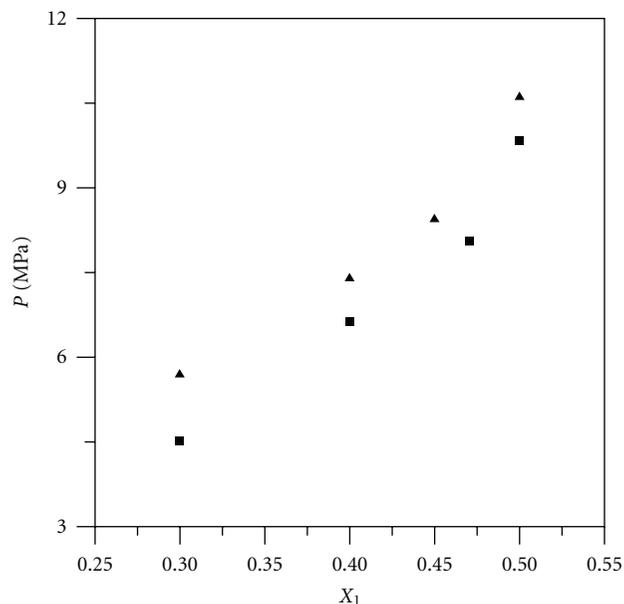


FIGURE 4: Phase transition Px diagram for the binary system $\text{CO}_2(1) + [\text{bmim}][\text{PF}_6](2)$ (■) and $\text{CO}_2(1) + [\text{bmim}][\text{PF}_6]_{\text{recovered}}(2)$ (▲) at 333 K.

disperse dye solubility in SCCO_2 using ionic liquids as an additive. This effect can be used to improve the color aspects in the textiles, one of the most desirable characteristics in the dyeing of textiles.

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