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Electro-oxidation of Benzyl Alcohol in a Biphasic System Consisting of Supercritical CO₂ and Ionic Liquids

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Electro-oxidation of benzyl alcohol was conducted by electrolysis in an ionic liquid/supercritical CO₂ (IL/SC CO₂) two-phase system in an undivided cell at 318.2 K and up to 10.3 MPa, and two ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]), were used as the solvents and electrolytes. It was demonstrated that benzyl alcohol could be efficiently electro-oxidized to benzaldehyde. [Bmim][BF₄] was more effective medium for the electro-oxidation of benzyl alcohol. The effects of various factors, such as pressure and the concentration of benzyl alcohol, on the reaction were studied as [Bmim][BF₄] was used. The Faradic efficiency (FE) and selectivity of benzaldehyde increased with the pressure of CO₂ when the pressure was lower than about 9.3 MPa, while the FE decreased as the pressure was increased further. This interesting phenomenon could be explained reasonably on the basis of solubility difference of the reactants and products. The experiments also indicated that the products could be easily recovered from the IL by using SC CO₂ extraction after the electrolysis, and the IL could be reused.

Introduction

The electro-organic synthesis has been pursued since the late 19th century. However, the electro-organic synthesis has not been fully developed compared with the thermally activated reaction except for a few excellent examples of successful electrolytic conversions in commercial organic chemistry (e.g., mucic acid electro-synthesis and the continued use of the adiponitrile process). There are several reasons for this, including the need of organic solvents/electrolytes in many situations, the limited solubility of reactants and products in typical electrolytes, the poor interphase mass transfer characteristics, the low selectivity and low efficiency for desired reaction products, and the requirement of the complex processing schemes.¹ Recently, electro-chemists have attempted to use nontraditional medium as electrolytes.²

In recent several years, ionic liquids (ILs) have generated much excitement among diverse sections of the chemistry community owing to their special physical and chemical properties, such as high stability, negligible vapor pressure, and nonflammability.^{3–7} ILs have been successfully applied to catalysis and noncatalysis reactions, separation processes, organic synthesis, and so on. The use of ILs as “green” alternatives to volatile organic solvents (VOS) offers great advantages to protect the environment and to limit hazardous emission problems in chemical plants or laboratories.⁸ In electrochemistry, ILs are also promising alternatives to traditional organic solvents or aqueous solvents because of their desirable properties. Their inherent ionic conductivity negated the requirement of extraneous electrolytes, which are often used in traditional solvents. ILs with a wide electrochemical window (>5 V) can also be obtained in the case of the combination of appropriate cation and anion. Moreover, the products or electrolytes (ILs here) can be easily recovered by distillation

or extraction and the traditional complex postprocess of products is simplified.^{8,9} However, an adverse factor for ILs in electrochemistry is their high viscosity, which limited the ion mobility and the mass transfer. Up to now, ILs have been used as versatile electrolytes in electroplating, rechargeable batteries, electropolymerization, photoelectrical cells, electrochemical devices, etc.^{2,10,11} Nevertheless, only two electro-organic reactions in ILs have been reported.^{9,12}

Supercritical fluids (SCFs) have also attracted considerable attention in diverse fields such as extraction and separation, chemical reaction, and material processing due to their favorable properties. For example, SCFs can be used as a reaction medium for chemical synthesis, which offers environmental and technical benefits.^{13,14} In electrochemistry, SCFs also have been used as solvents since the 1980s.^{1,2} When SC CO₂ is used as solvent in electro-organic synthesis, it has several advantages, such as increasing mass transfer rates, simplifying the post-product process, and tuning the product selectivity by changing pressure.¹ However, electrochemistry in SC CO₂ has still been restricted to the study of simple redox systems such as ferrocene.^{2,15} Major problems encountered are the limited solubility of counter electrolytes and high association of ions in nonpolar SC CO₂, which has blocked the development of electrochemistry in SC CO₂.^{16,17}

Interest in the study of the two-phase system consisting of SC CO₂ and ILs, which are at the two ends of the volatility and polarity scales, has increased since 1999.^{18,19} Some successful applications of this concept have been reviewed and reported.^{20–25} Several examples have shown that the biphasic systems of ILs and SC CO₂ can offer much more potential for process optimization due to easy separation of reactants, catalyst, and products.^{21–25} Some studies about electrochemical properties of the two-phase system were carried out recently by our group. The results are encouraging. For example, a large amount of CO₂ dissolved in ionic liquids can enhance the conductivity and ion mobility of ionic liquids and reduce the viscosity.^{26,27} When

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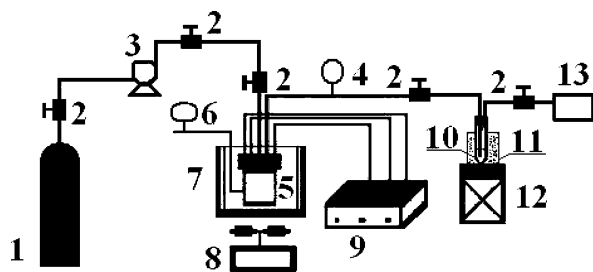


Figure 1. Electrolytic experimental apparatus: 1, CO₂ cylinder; 2, valve; 3, syringe pump; 4, pressure gauge; 5, high-pressure electrolysis cell; 6, thermometer; 7, constant temperature air bath; 8, stirrer; 9, potentiostat–galvanostat; 10, cold trap; 11, mixture of ice and salt bath; 12, elevator table; 13, gas bag.

a small amount of water exists, the CO₂ can be successfully reduced in ILs.²⁸ On the basis of the preliminary investigations, several potential advantages are expected for electrochemical oxidation in the two-phase system composed of IL and SC CO₂. First, the selectivity of the products may be tuned by controlling the pressure of compressed CO₂. Second, the complex process of collecting products accompanying the traditional electro-organic synthesis is simplified because products can be collected in situ by SC CO₂ extraction. Finally, the electrolyte can be recycled and reused. Therefore, the two-phase system of SC CO₂ and ILs is expected to make use of their advantages and avoid their shortcomings when used separately in electro-organic synthesis.

The oxidation of an aromatic alcohol into its corresponding aldehyde is an important transformation because aromatic aldehydes are versatile intermediates for the production of pharmaceuticals, plastic additives, and perfumes.^{29–34} However, a major drawback of such oxidation reactions is their lack of selectivity owing to the easy over-oxidation of aldehydes into carboxylic acids since aldehydes are more readily amenable to oxidation than aromatic alcohols. Extensive investigation of the oxidation of benzyl alcohol was conducted to improve the aldehyde selectivity in catalyst reactions and electro-organic reactions since benzaldehyde is the simplest representative of aromatic aldehydes.^{29,30,33,34} Moreover, considerable improvement of selectivity to benzaldehyde was recently reported when the oxidation of benzyl alcohol was carried out in SC CO₂ or ionic liquids.^{29,32,33} In this paper, we select the electro-oxidation reaction of benzyl alcohol as a model reaction to investigate the potential advantages related to electro-organic synthesis in the biphasic system of ILs and SC CO₂.

Experimental Section

Chemical Reagents. 1-Methylimidazole (99% in purity) was used as received from ACROS Organics. 1-Chloride-*n*-butane, methanol, and benzyl alcohol supplied by Beijing Chemical Reagent Factory were A. R. grade. CO₂ (>99.995%) was provided by the Beijing Analytical Instrument Factory. The ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]), were synthesized according to the procedures in the literature.^{35,36} The IL was dried under vacuum at 50 °C until the weight remained constant with drying time. It was characterized with IR and ¹H NMR.^{35,36}

Apparatus. The apparatus used in this work was similar to that described in our previous paper,²⁸ and its schematic diagram is shown in Figure 1. It consisted mainly of a syringe pump, a high-pressure electrolysis cell, a potentiostat–galvanostat (CMBP-1), a pressure gauge, a constant air bath, a magnetic stirrer, and

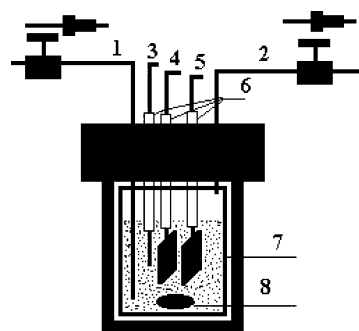


Figure 2. Structure of the high-pressure electrolytic cell: 1, gas inlet; 2, gas outlet; 3, quasi-reference electrode (Pt wire, not used in this work); 4, cathode (Cu plank); 5, anode (Pt plank); 6, Teflon packing; 7, Teflon; 8, stirrer.

a cold trap. The internal structure of the high-pressure electrolysis cell is demonstrated in Figure 2. It was composed mainly of a Teflon-lined stainless steel cell of 30 mL, a Cu (>99.99%) plank cathode, a Pt (>99.99%) plank anode, and Pt wire quasi-reference electrode with a diameter of 0.3 mm. Both the Cu cathode and Pt anode had geometric areas of 2.0 cm². They were arranged in parallel, and the distance between them was 3 mm. The liquid in the cell was stirred by using a magnetic stirrer.

Experimental Procedures. In a typical experiment, the electrodes were electrochemically etched in concentrated H₃-PO₄ before the reaction, rinsed with double-distilled water and methanol, and then dried. A certain amount of IL, benzyl alcohol, and water were added into the electrolysis cell. In all of the experiments, the original liquid height of reaction system was the same before CO₂ was charged. The cell was sealed, and, at the same time, the three electrodes were immersed into the IL because they were fixed on the cover of the cell. CO₂ was charged into the cell up to 3 MPa, and then the CO₂ was released to atmospheric pressure. This was repeated three times so that the air in the cell was replaced by CO₂. The electrolysis cell was placed into the constant temperature air bath of 318.2 K, CO₂ of desired pressure was compressed into the electrolysis cell, and the stirrer was started. The system was equilibrated at desired pressure for at least 8 h. Then the electrolysis was conducted galvanostatically (the current density was 10 mA/cm²). After the electrolysis, the gaseous products were released slowly to pass through the cold trap and collected with a gasbag. Subsequently, the liquid products were extracted from the IL with SC CO₂ at 12 MPa. The IL could be reused after drying. The concentration of the IL in the extracted product was determined by ¹H NMR (Bruker A. M. 300). To do this, we first determined the spectra of the prepared solutions with IL concentrations of 1, 0.1, 0.05, and 0.01 wt %, respectively. The results indicated that the characteristic peaks of the ionic liquid in 1, 0.1, and 0.05 wt % solutions could be observed, while the characteristic peaks of the IL in the extracted products were not observed, indicating that the concentration of the IL in the extracted products was smaller than 0.05 wt %. The concentration of the IL in the products was very low because the solubility of the IL in SC CO₂ was negligible.^{18,19}

Gaseous product was analyzed by a GC (Agilent 4890 D, Agilent Technologies) equipped with a carbon sieves packing column and TCD detector for CO, O₂, H₂, and hydrocarbon. CO, O₂, and H₂ were detected. The liquid products were analyzed with a GC equipped with a capillary column (Innowax, 30 m × 0.25 mm), FID detector, and GC–MS (Micromass UK).

TABLE 1: Effect of Water and the Type of Ionic Liquids on the outcome of the Reaction^a

entry	H ₂ O (g)	conversion of BA ^b (%)	selectivity of BD ^c (%)	FE for BD ^d (%)	others on the electrode
1	0				yellow film
2	0.25				yellow film
3	0.35	6.1	96.8	29.3	nothing
4	0.55	7.3	97.8	23.5	nothing
5	0.35	9.5	99.2	35.4	nothing

^a Experimental conditions: $T = 318.2$ K, $P = 8.8$ MPa; the weight of benzyl alcohol added is 2.2 g; the current density (I) is 10 mA/cm²; entries 1–4, the molar ratio of benzyl alcohol to [Bmim][PF₆] = 1:2.09; entry 5, the molar ratio of benzyl alcohol to [Bmim][BF₄] = 1:2.38; passed charge 936 C. ^b Conversion of benzyl alcohol. ^c Selectivity of benzaldehyde. ^d Faradic efficiency for benzaldehyde (%).

Results and Discussion

Effect of Water Amount and Type of ILs on Reaction.

Water may play an important role in the electro-organic synthesis in the two-phase IL/CO₂ system. The presence of a water molecule may affect the electrochemical potential of reactants. For example, the E° for the reduction of CO₂ in the dry dimethylformamide (DMF) is -2.21 V (SCE); the value in water is -0.2 V (SHE).^{37,38} The presence of a suitable amount of water may favor the oxidation of benzyl alcohol, and affect the outcome of anode reaction and the selectivity of products.^{34,38,39} However, large amounts of added water often lead to pronounced side reactions such as the generation of O₂ and/or H₂. It would restrain the carry-through of the model reaction, waste a large amount of energy, and disobey the high efficiency and economic principle of green chemistry. Therefore, we first investigated the effect of the amount of water on the reaction. The experimental results are shown in Table 1. The Faradic efficiency (FE) for species i was defined as¹²

$$FE(i) = \frac{Q_T(i)}{\sum Q_P} \quad (1)$$

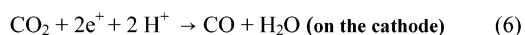
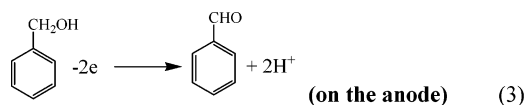
where $Q_T(i)$ and $\sum Q_P$ stand for the theoretical charge of the substance i and the total charge passed, respectively.

In the liquid product, only the desired product benzaldehyde and a small percentage of benzyl ether was detected (as for how benzyl ether was produced is not clear). Therefore, the selectivity of benzaldehyde is defined by the following equation

$$Sel_{BD} = \frac{X_{BD}}{X_{BD} + X_{BE}} \times 100\% \quad (2)$$

where X_{BD} and X_{BE} stand for the mole fractions of benzaldehyde and benzyl ether in the product, respectively.

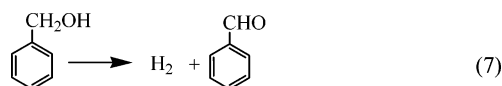
In the gaseous products, CO, H₂, and O₂ were detected. Therefore, some possible reactions at the surfaces of the electrodes are formulated as follows^{17,40,41}:

**TABLE 2: Effect of the Concentration of Benzyl Alcohol on the Electrolysis^a**

entry	RHB ^b	IL (g)	BA ^c (g)	MRBL ^d	FE for BD ^e (%)	selectivity of BD ^f (%)
1	0.95	11.1	2.23	0.23	35.4	99.2
2	0.47	9.78	4.53	0.40	43.5	96.5
3	0.33	7.17	6.41	0.54	42.5	91.6
4	0.28	5.72	7.58	0.61	40.6	95.4

^a Experimental conditions: $P = 8.8$ MPa, water 0.35 g; the current density is 10 mA/cm²; passed charge 936 C. ^b The molar ratio of added water to benzyl alcohol. ^c BA = benzyl alcohol. ^d MRBL is the molar ratio of benzyl alcohol to the total moles of the liquid compounds (including water, ionic liquid, and benzyl alcohol). ^e Faradic efficiency for benzaldehyde (%). ^f Selectivity of benzaldehyde.

The whole chemical reaction equation for the electro-oxidation of benzyl alcohol to benzaldehyde can be expressed as



and the side reaction can be written as



The reactions at the surfaces of the electrodes are very complex, and it is very difficult to give more detailed discussion about this. In this paper, we concentrate on how different factors affect the FE and selectivity for benzaldehyde.

The oxidation products of benzyl alcohol varied largely when the amount of water increased from 0 to 0.55, as shown in Table 1. When the amount of water is smaller than 0.25, the main product is a yellow membrane on the electrode. This film is nonconductive, which was evidenced by the fact the cell voltage increased sharply after the electrode was covered completely by the film. When the amount of H₂O was larger than 0.35 g, no film was formed on the electrode, as is also shown in Table 1. However, the FE of benzaldehyde dropped down when the amount of added water increased further to 0.55 g.

By comparing entries 3 and 5 in Table 1, it can be shown that [Bmim][BF₄] is a more effective medium for the oxidation of benzyl alcohol. Hence, the effects of reactant concentration and pressure on electrolysis using [Bmim][BF₄] as solvent and electrolyte were studied further, which are discussed in the following sections.

Effect of the Concentration of Benzyl Alcohol on the Faradic Efficiency of Products. The effect of the concentration of benzyl alcohol on the Faradic efficiency and the selectivity of products was also investigated, and the results are shown in Table 2.

The FE of benzaldehyde first increased with the concentration of benzyl alcohol when the MRBL (the molar ratio of benzyl alcohol to the total moles of the liquid compounds) changed from 0.23 to 0.40 and then dropped slowly as the MRBL varied from 0.54 to 0.61. One of the reasons was that suitable amount of water promoted the generation of benzaldehyde as discussed above. However, when too much water was added (for example, entry 1), side reactions, such as the generation of O₂ and H₂, competed with the generation of benzaldehyde. Hence, the FE of benzaldehyde was smaller. On the other hand, the FE of benzaldehyde was also smaller as the amount of water was not enough (the mole fraction of benzyl alcohol was too large).

Effect of the Pressure of CO₂ on the Faradic Efficiency and Selectivity of Products. A series of experiments were also

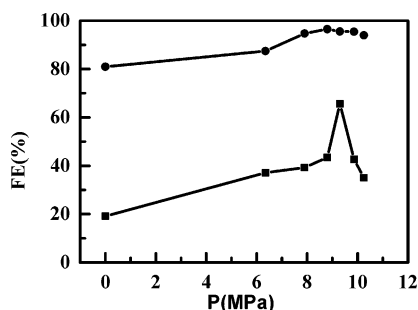


Figure 3. Effect of pressure of CO_2 on the Faradic efficiency and the selectivity of the benzaldehyde: (■) FE of benzaldehyde; (●) selectivity for benzaldehyde. Reaction conditions: water 0.35 g, [Bmim][BF_4] 9.78 g, benzyl alcohol 4.53 g, $I = 10 \text{ mA/cm}^2$, passed charge 936 C.

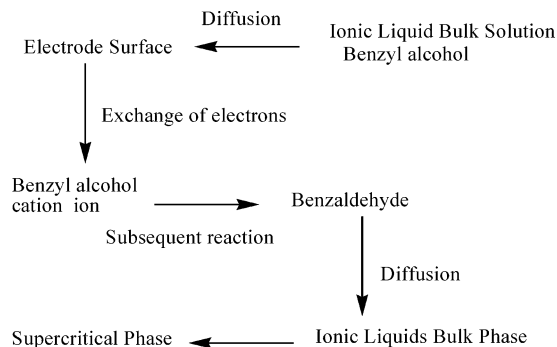


Figure 4. Schematic diagram of the process of the formation of benzaldehyde.

conducted to study the effect of pressure on the selectivity and FE of the products. The results are shown in Figure 3. The FE of benzaldehyde increased with pressure at first, and then decreased, and the maximum occurred at about 9.3 MPa. This phenomenon can be explained from two aspects: one from the actual course and specialty of a heterogeneous electro-organic reaction and the other from special physicochemical properties of SCFs, which are discussed in the following text.

A heterogeneous reaction often involves three basic steps: (1) Transfer of electro-active species from the bulk of the solution to the electrode surface, namely the diffusion process. (2) The adsorption of electro-active species on the electrode surface and exchange of electrons between electrode and species. (3) Desorption and removal of the primary electrode products from the electrode surface. For the formation of benzaldehyde, the process of electro-organic synthesis may be described schematically in Figure 4.

Benzyl alcohol diffuses to the surface of working electrode from the bulk solution of ILs. And then it loses two electrons to form the benzyl alcohol cation. The final product diffuses into the ionic liquids bulk phase and then distributes between the liquid phase and SC CO_2 phase.

For a system of heterogeneous electrochemical reaction, the nature of the working electrode, the electrode potential (or current density), the nature and viscosity of the medium and electrolyte, the concentration of reactants and products, and mass transfer coefficients and so on can determine the overall rates and the selectivity of products if there are several parallel reactions.⁴¹ For the data in Figure 3, the working electrode is fixed, and the amount of added reactants and medium (including water, ionic liquid, and benzyl alcohol) was the same at all pressures. The current density of system was also fixed (10 mA/cm^2). For this system, the concentrations of all of the substances (include H_2O , benzyl alcohol, benzaldehyde, CO_2) in the IL phase and relative concentration changes can be expected to

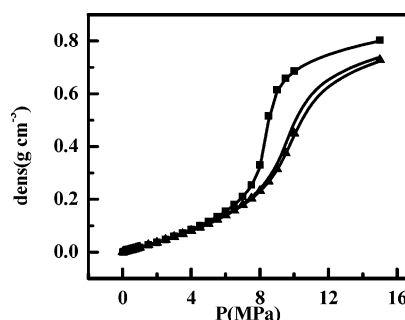


Figure 5. Density of CO_2 at different pressures and temperatures: (■) density at 310 K, (▲) density at 320 K (data taken from the literature⁴⁴), (—) density calculated by PR equation at 310, 318.2, and 320 K, respectively.

determine FE and the selectivity. When the pressure of CO_2 changes from atmosphere to 10.3 MPa while all the other conditions are fixed, the relative concentration changes of reactants and products in the IL phase with the increase of CO_2 pressure may be the major reason for the changes of the FE of benzaldehyde and the selectivity.

Although the whole system is not in thermodynamic equilibrium in the electrolytic process due to diffusion limitation, the trends of concentration changes can be analyzed qualitatively in terms of thermodynamics.⁴² An important thermodynamic property is the distribution coefficient, K_i , the ratio of the mole fraction (y) or concentration (c) of substance i in SC CO_2 phase and IL phase.

$$K_i = \frac{y_i^{\text{CO}_2}}{y_i^{\text{IL}}} \text{ or } K_i = \frac{c_i^{\text{CO}_2}}{c_i^{\text{IL}}} \quad (9)$$

As known from the above equation, the value of c_i^{IL} is in inverse proportion with that of K_i . The value of K_i is not only affected by the properties of substance i but also strongly dependent on the temperature and pressure of the system because the solvent power of SC CO_2 is sensitive to temperature and pressure.⁴³ According to Brennecke and co-workers,⁴² the liquid organic solutes with high polarities and low volatility should have a large affinity for the IL phase and a low affinity for CO_2 , giving small K_i values. Conversely, nonpolar and high volatility solutes should have a greater affinity for CO_2 , resulting in larger K_i values. Therefore, high volatility and low polarity will favor the dissolution of a solute in CO_2 phase. In contrast, high polarity and low volatility will favor the dissolution in the IL-rich liquid phase. Thus, it can be expected that the distribution coefficient of benzylaldehyde ($K_{\text{benzylaldehyde}}$) should be larger than that of benzyl alcohol ($K_{\text{benzylalcohol}}$) at the same temperature and pressure because of the stronger polarity and lower volatility of benzyl alcohol.

The value of K_i should increase as the pressure increases due to the enhancement of solvent power of SC CO_2 . The solvent power of a SCF is directly related to its density.⁴³ The density of CO_2 at different pressures is shown in Figure 5, which was taken from the literature.⁴⁴ As shown in the Figure 5, the experimental values at 310 and 320 K agree very well with those calculated in this work by PR equation of state.⁴⁵ Then the density data at 318.2 K was calculated. A sharp increase for the density of CO_2 occurs in the vicinity of 9.3 MPa at 318.2 K; i.e., the solvent power of CO_2 should be enhanced substantially.

The solubility of benzyl alcohol and benzaldehyde in SC CO_2 also provide profound evidence to the sharp increase of its

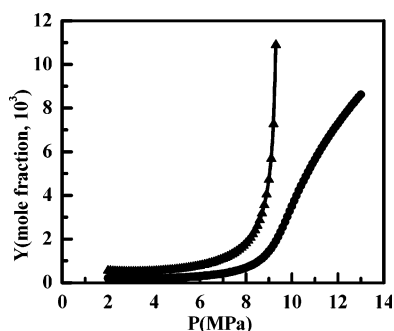


Figure 6. Solubility of benzaldehyde and benzyl alcohol in CO₂ with different pressures at 318.2 K: (▲) benzaldehyde, (●) benzyl alcohol.

TABLE 3: Physical Properties for the Pure Component and Binary Interaction Coefficients

compd	T_c^a (K)	P_c^a (MPa)	ω^a	K_{ij}	E_{ij}
carbon dioxide	304.3	7.38	0.239		
benzyl alcohol	447.0	4.40	0.351 ^b	0.135	0.0
benzaldehyde	421.8	4.54	0.316	0.041	-0.029

^a Taken from ref 9. ^b Taken from ref 47.

solvency at about 9.3 MPa and 318.2 K, which is shown in Figure 6. These data were also calculated from the PR equation.⁴⁵ The critical properties, acentric factors, and binary interaction parameters required in the calculation are given in Table 3. The binary interaction parameters were acquired by fitting the solubility data of benzyl alcohol and benzaldehyde reported in the literatures at 313 and 333 K, respectively.^{46–48} The absolute average deviation between the experimental and calculated solubility data was less than 7%.

Figure 6 shows that the solubilities of benzyl alcohol and benzaldehyde increase sharply with increasing pressure as the pressure reaches certain values, and it can be expected that K_i also increases with pressure. However, the variation of solubility or K_i of different species with pressure is different, as shown in Figure 6. Similar behavior was also reported for other systems. For example, Wagner et al. reported that at 323 K the distribution coefficient of benzaldehyde in two-phase mixture of SC CO₂ and water increased from 3.2 to 13.5 when the pressure increased from 8.34 to 10.53 MPa, while that of benzyl alcohol increased from 0.26 to 1.72 when the pressure increased from 8.1 to 10.3 MPa.⁵⁰ Figure 6 illustrates that in the whole pressure range (from 1 to 13 MPa), the solubility of benzaldehyde in CO₂ is larger than that of benzyl alcohol. At about 9 MPa, there is a sharp increase for the solubility of benzaldehyde in CO₂. In contrast, the enhancement of the solubility of benzyl alcohol was relatively small. The solubility of benzyl alcohol increase faster at pressures higher than about 9.3 MPa.

The significant effect of CO₂ pressure on the solubility or K_i of benzaldehyde and benzyl alcohol is crucial for the variation of FE and selectivity of benzaldehyde with changing CO₂ pressure. When the solubility of benzaldehyde in SC CO₂ increased dramatically, more benzaldehyde produced entered SC CO₂ phase, and thus the FE and selectivity of benzaldehyde were enhanced. When the pressure reached a certain value, the solubility of benzyl alcohol (the reactant) in SC CO₂ also increased considerably, which was not favorable to producing benzaldehyde. When the pressure was lower than 9.3 MPa, the first factor was dominant and thus the FE and selectivity of benzaldehyde increased with pressure. However, when the pressure was larger than about 9.3 MPa, the second factor became dominant. Therefore, a maximum value in FE occurred

TABLE 4: Recovery and Reuse of the Ionic Liquid at 318.2 K and 8.8 MPa^a

run	benzaldehyde FE (%)	selectivity of benzaldehyde (%)
1	43.5	96.5
2	42.3	94.7
3	44.5	97.4
4	41.0	96.0

^a Experimental conditions: weight of water 0.35 g, [Bmim][BF₄] 9.78 g, benzyl alcohol 4.53 g, $I = 10$ mA/cm², passed charge 936 C.

(see Figure 3). Moreover, the solubility of water in SC CO₂ changed a little in the experimental pressure range due to its high polarity.⁵¹ As shown in Figure 3, the selectivity is not sensitive to pressure as the pressure is high enough. This is easy to understand because most benzaldehyde produced entered SC CO₂ phase under these conditions.

It should be emphasized that the phase behavior of the reaction system was just one of the factors used to influence the FE and the selectivity. Other factors, such as the viscosity and conductivity of the ionic liquid-rich phase, changed with CO₂ pressure,^{26,27} which should also affect the reaction.

Recovery and Reuse of IL. The easy recyclization is one of the advantages for the utilization of ionic liquids. The experiments to use IL repeatedly were conducted at 8.8 MPa, and the amount of water in the reaction system was 0.35 g. After reaction, the chemicals were recovered by extraction using SC CO₂, and IL was left in the electrolysis cell after the extraction process. The IL was reused for the next run after drying. The results are listed in Table 4. The ionic liquid in the extracted product was negligible because the solubility of the ionic liquid in SC CO₂ was negligibly small.^{18,19} Obviously, the IL can be reused at least three times without changing the FE and selectivity of the product considerably. The IR and ¹H NMR studies indicated that a change in the IL before and after being used three times was not detectable.

Conclusions

In summary, the concept of combining SCFs and IL is realized in the field of electro-organic synthesis, and electro-oxidation of benzyl alcohol to benzaldehyde was conducted in the CO₂/IL system. There are some unique advantages for this process. For example, the selectivity of the products could be tuned by varying the CO₂ pressure. The IL can be easily reused after in situ extraction of the product by using SC CO₂. There is a maximum in the FE vs pressure curve at about 9.3 MPa, which can be explained partially by the phase behavior of the electrolysis system. The combination of nonvolatile ILs, non-hazardous SC CO₂, and clean electrochemical technology may provide more efficient and cleaner methods to produce benzaldehyde or even some other valuable chemicals.

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Appendix

The Peng–Robinson equation⁴⁵ was used to calculate the vapor–liquid equilibrium data, which is expressed as

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \quad (10)$$

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha \quad (11)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (12)$$

$$\alpha = [1 + m(1 - \sqrt{TT_c})]^2 \quad (13)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (14)$$

For a mixture, the Van der Waals mixing rules are applied

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (15)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (16)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_{ii} a_{jj}} \quad (17)$$

$$b_{ij} = (1 - E_{ij}) \sqrt{b_{ii} b_{jj}} \quad (18)$$

where T_c , P_c , and ω stand for the critical temperature, critical pressure, and acentric factor, respectively. k_{ij} , E_{ij} is the binary interaction coefficient. In this work, k_{ij} , E_{ij} of CO₂–benzyl alcohol and CO₂–benzaldehyde were obtained by correlating vapor–liquid equilibrium data of the binary mixtures reported in the literature.^{46–48}

References and Notes

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