Phase Separation of the Reaction System Induced by CO₂ and Conversion Enhancement for the Esterification of Acetic Acid with Ethanol in Ionic Liquid

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The effect of CO_2 on the phase behavior of the reaction system and equilibrium conversion for esterification of acetic acid and ethanol in ionic liquid (1-butyl-3-methylimidazolium hydrogen sulfate, [bmim][HSO₄]) was studied at 60.0 °C up to 15 MPa. It was demonstrated that there was only one phase in the reaction system in the absence of CO_2. The reaction system underwent two-phase→three-phase→two-phase transitions with increasing pressure. The pressure of CO_2 or the phase behavior of the system affected the equilibrium conversion of the reaction markedly. As the pressure was less than 3.5 MPa, there were two phases in the system, and the equilibrium conversion increased as pressure was increased. In the pressure range of 3.5—9.5 MPa, there existed three phases, and the equilibrium conversion increased more rapidly with increasing pressure. As the pressure was higher than 9.5 MPa, the reaction system entered another two-phase region and the equilibrium conversion was nearly independent of pressure. The total equilibrium conversion was 64% without CO_2 and could be as high as 80% as pressure was higher than 9.0 MPa. The apparent equilibrium constants (K_x) in different phases were also determined, showing that the K_x in the middle phase or top phase was much greater than that in the bottom phase.

Introduction

Ionic liquids (ILs) are organic salts, which are liquids at ambient temperature. They have some excellent properties, such as extremely low vapor pressure, high thermal stability, non-flammability, and tunable solvent power for organic and inorganic compounds.[1] Study on the properties and applications of ILs have received much attention in recent years.[2] Reactions in ILs are one of the interesting topics, and many reactions have been carried out using ILs as reaction media or catalysts.[3]

Supercritical fluids (SCFs) have also attracted considerable attention in diverse fields because of their favorable properties. Supercritical CO_2 (scCO_2) is the most attractive because it is nontoxic, nonflammable, inexpensive, readily available in large quantities, and has moderate critical temperature and pressure (31.1 °C and 7.38 MPa). scCO_2 has been utilized in many chemical processes, such as extraction and fractionation,[4] chemical reactions,[5] and material processing.[6]

Both ILs and scCO_2 are green solvents, but their properties are very different because they are at the two ends of the volatility and polarity scales. The combination of them may have some unique features. It has been discovered that scCO_2 is soluble in ILs, while the solubility of ILs in scCO_2 is negligible.[7] scCO_2 has been used to extract substances from ILs,[8] including extraction of products after reactions in ILs.[9] This method can avoid cross-contamination because of the insoluble nature of ILs in scCO_2. Some IL/scCO_2 biphasic systems have been used for different chemical reactions as reaction media.[10] Our previous work demonstrated that the selectivity of Wacker oxidation reaction in the IL/scCO_2 biphasic system was higher than those in IL or scCO_2,[11] and the equilibrium conversion of the transesterication reaction of isoamyl acetate and ethanol could be tuned by pressure.[12]

Brennecke and co-workers found that compressed CO_2 could induce phase separation of [bmim][PF₆]/methanol mixture.[13] In the absence of CO_2, only one phase existed in the system, and there could be two phases or three phases after adding CO_2. At suitable conditions, the IL and methanol could be separated completely. Recently, several papers have been published to study the phase behaviors of different ternary systems which contain both CO_2 and ILs.[14]

Enhancing equilibrium conversion of reversible reactions has been a topic of great importance for a long time. In this work, we study the phase separation of the reaction system for the esterification of acetic acid with ethanol in [bmim][HSO₄] induced by CO_2, which in turn enhances the equilibrium conversion of the reversible reaction. This reaction is selected because it is a typical reversible reaction and has been studied extensively. Therefore, we can focus on how CO_2 induces the phase separation of the reaction system and affects equilibrium conversion. It is demonstrated that there is one phase in the reaction system in the absence of CO_2. The system undergoes two-phase→three phase→two phase transition as the pressure of CO_2 is increased, and the equilibrium conversion changes considerably as the phase behavior changes. We believe that using CO_2 as a green additive to induce phase separation of the reaction in ILs and to enhance the reaction efficiency have potential applications.

Experimental Section

Materials. CO_2 with a purity of 99.995% was supplied by Beijing Analytical Instrument Factory. 1-Methylimidazole was purchased from Aldrich. All other chemicals (A. R. grade) were produced by Beijing Chemical Reagent Plant and were used without further purification unless stated. 1-Butyl-3-methylimidazolium chloride ([bmim]Cl) was first synthesized according to the procedures described in the literature.[15] Then, [bmim]-

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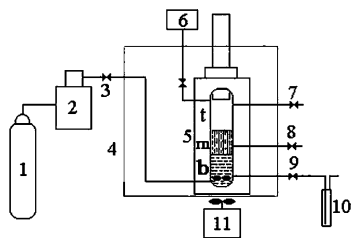

Figure 1. Schematic diagram of the apparatus. 1, CO_2 reservoir; 2, computer-controlled metering syringe pumps; 3, 7, 8, 9, valves; 4, constant temperature water bath; 5, optical cell; 6, pressure gauge; 10, cold trap; and 11, magnetic stirrer.

[HSO$_4$] was prepared by a dropwise addition of one equivalent of concentrated sulfuric acid (98%) to a cooled solution of [bmim]Cl in anhydrous dichloromethane as described in the literature.[16] The mixture was refluxed for 48 h and the byproduct HCl formed in the reaction was carried out of the condenser under a stream of dry nitrogen and was dissolved in deionized water at 0 °C. When the formed HCl had been completely removed, CH_2Cl_2 was evaporated with a rotary evaporator. The IL was dried under vacuum at 70 °C for 6 h and was stored in a desiccator.

Apparatus. The schematic diagram of the apparatus is shown in Figure 1. It was composed mainly of a CO_2 cylinder, computer-controlled metering syringe pumps, a constant temperature water bath, a pressure gauge, a volume-variable optical cell, a magnetic stirrer, and a cold trap. The volume of the optical cell could be changed in the range from 23 to 50 cm^3 by moving the piston. The constant-temperature water bath was controlled by a Haake-D8 temperature controller, and the temperature was determined by an accurate mercury thermometer with the accuracy of better than ±0.05 K. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT Model 93) and an indicator. Its accuracy was ±0.025 MPa in the pressure range of 0−20 MPa.

Procedures to Determine the Total Conversion. The IL acts both as solvent and catalyst in the reaction. In a typical experiment, 0.017 mol of [bmim][HSO$_4$], 0.085 mol of acetic acid, and 0.085 mol of ethanol (4.00, 3.92, and 5.10 g, respectively) were loaded into the optical stainless-steel cell, and the volume of the cell was fixed at 50 cm^3. The cell was placed in a constant-temperature water bath, and then CO_2 was charged into the system using the high-pressure pump to a certain pressure, and the reaction proceeded at constant pressure. After the desired reaction time, the cell was placed in an ice bath and CO_2 was released slowly. Experiments showed that the reactants and the products entrained by the released CO_2 were negligible. The analysis of the product was performed on a gas chromatographer (Agilent 4890D).

Procedures to Determine the Conversions in Different Phases. In this work, the conversions in different phases were also determined by separate experiments. The procedures to charge the chemicals were the same as described above. However, the samples in different phases were taken and analyzed separately. To sample the bottom phase, valve nine was opened slowly, and some of the mixture in the bottom phase entered the cold trap which was filled with *N,N*-dimethyl formamide (DMF). At the same time, the volume of the optical cell was adjusted by moving the piston to keep the pressure unchanged. CO_2 passing through the cold trap was collected in a gasbag, and the amounts were determined by a volumetric method.[14c] Valve nine was closed after a suitable amount of sample was taken. The mass of the solution in the cold trap was known gravimetrically. The concentrations of reactants and

products in DMF solution were measured by the gas chromatographer (Agilent 4890D), and their amounts were gotten from the mass of the solution and their concentrations. Using a similar procedure, middle phase and top phase samples were collected, respectively.

Results and Discussion

General Principle. The idea of this work is that the reaction system is a single phase without CO_2. All the reactants and products exist in the same phase and the equilibrium conversion is fixed at fixed temperature and pressure. There can be two or more phases after CO_2 is added, and the equilibrium conversion may be changed considerably. For the sake of simplicity, we use the esterification reaction of ethanol and acetic acid as the example to discuss the principle. The reaction can be expressed using the following equation.

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O \tag{1}$$
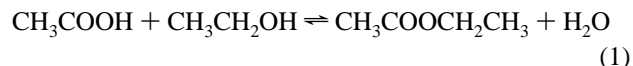
For the esterification reaction, the thermodynamic equilibrium constant (K_a) can be expressed by the following equation.

$$K_a = \frac{\gamma_c x_c \gamma_d x_d}{\gamma_a x_a \gamma_b x_b} = K_\gamma K_x \tag{2}$$

and

$$K_\gamma = \frac{\gamma_c \gamma_d}{\gamma_a \gamma_b} \tag{3}$$

$$K_x = \frac{x_c x_d}{x_a x_b} \tag{4}$$

where x_a, x_b, x_c, and x_d are mole fractions of acetic acid, ethanol, ethyl acetic, and water at equilibrium condition, respectively. γ_a, γ_b, γ_c, and γ_d are the corresponding activity coefficients. K_x is the apparent equilibrium constant. At equilibrium condition, both chemical equilibrium and phase equilibrium are reached. Therefore, K_a is independent of pressure and the values in all the phases should be the same, because on the basis of criteria of phase equilibrium, the activity ($\gamma_i x_i$) of each component in the different phases should be the same. However, the activity coefficients of each component in the different phases can be different significantly depending on pressure. It can be known from eqs 2−4 that K_x, which is closely related with the equilibrium conversion, in different phases can be different considerably. Thus, the equilibrium conversion can be tuned by changing phase behavior or pressure.

Effect of Reaction Time on the Total Conversion of Ethanol. The conversion of ethanol is defined as the ratio of the reacted moles of ethanol to original moles of ethanol. In this work, all the experiments were conducted at 60 °C. Figure 2 shows the variation of ethanol conversion with reaction time at some selected pressures. It can be seen from the figure that the equilibrium of the reaction can be reached within 20 h in the pressure range studied. Longer equilibration time is required in the presence of CO_2. The main reason is that there are two or three phases in the system as CO_2 is added, which will be discussed in the following section, and the mass transfer between phases results in long equilibration time.

Phase Behavior and Total Equilibrium Conversion of Ethanol. To determine the total equilibrium conversion, the reaction time was at least 20 h in the experiments. The phase
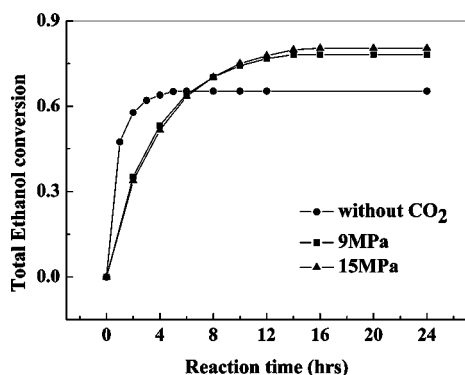
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Figure 2. Dependence of ethanol conversion in [bmim][HSO$_4$]/CO$_2$ system on reaction time at 60 °C.
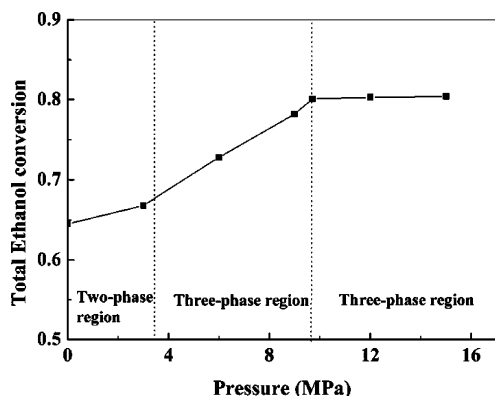

Figure 3. Effect of pressure on ethanol conversion in [bmim][HSO$_4$]/CO$_2$ system at 60 °C.

behaviors of the reaction system at equilibrium conditions were also observed simultaneously. There are two phases when the pressure is less than 3.5 MPa. The liquid phase separates into two liquid phases as the pressure is higher than 3.5 MPa. With further increase of the pressure, the middle phase expands greatly, and it fills the whole space above the bottom liquid phase when the pressure is higher than 9.5 MPa, that is, there are two phases in the system at this condition. The reaction system undergoes two phases→three phases→two phases transition in the pressure range studied.

Figure 3 shows the dependence of total equilibrium conversion of ethanol in the system on pressure. In the first two-phase region (<3.5 MPa), the conversion increases slowly with the increase of pressure. In the three-phase region (3.5−9.5 MPa), the conversion increases more rapidly with increasing pressure. Then, the conversion keeps almost constant as the pressure is increased further. It can be seen from Figure 3 that the influence of pressure on ethanol conversion in the three-phase region is greater than that in the two-phase regions.

K_x in Different Phases. To understand the effect of phase behavior on the conversion, the equilibrium mole ratios of the reactants and products in different phases were determined separately. The molar ratios of ethanol:acetic acid:ethyl acetate: water in different phases are given in Table 1. The mole ratios of the components in vapor phase (top phase) at 3 and 6 MPa were not determined because at these pressures the concentrations of the components are very low because of very weak solvent power of CO$_2$ at these conditions. For example, the mole fractions of ethyl acetic, which is the most volatile component, in the vapor phase at 3.0 and 6.0 MPa are 0.007 and 0.016, respectively. Therefore, it was very difficult to get reliable data. Table 1 shows that the reactants and products are distributed in
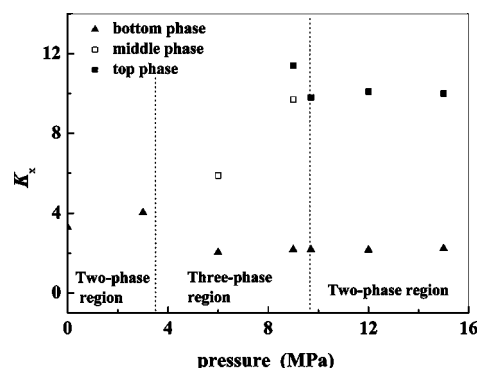

Figure 4. K_x in different phases at 60 °C and different pressures.

TABLE 1: The Mole Ratios of Reactants and Products in Different Phases at 60 °C and Different Pressures (Ethanol:Acetic Acid:Ethyl Acetic:Water)

P/MPa	bottom phase	middle phase	top phase
0	0.55:0.55:1:1	no middle phase	
3.0	0.50:0.50:1:1	no middle phase	
6.0	0.26:0.35:0.18:1	0.29:0.17:1:0.28	
9.0	0.14:0.20:0.06:1	0.19:0.11:1:0.20	0.60:0.037:1:0.26
9.5	0.085:0.17:0.033:1	no middle phase	0.16:0.14:1:0.22
12.0	0.15:0.26:0.082:1	no middle phase	0.16:0.13:1:0.21
15.0	0.15:0.28:0.091:1	no middle phase	0.15:0.14:1:0.21

different phases. However, this does not happen as the reaction is conducted in [bmim][HSO$_4$].

According to the data in Table 1, K_x in different phases at different pressures was calculated. The dependence of the K_x on phase behavior is shown in Figure 4. As can be seen from the figure, K_x in the middle phase is much greater than that in the bottom phase and is similar to that in the top phase at pressures higher than 9.5 MPa. K_x in the bottom phase is nearly independent of pressure as the pressure is higher than 3.5 MPa.

There are two phases in the reaction system at pressures lower than 3.5 MPa. The solubility of CO$_2$ in the liquid phase increases as pressure rises, which affects the activity coefficients of the components, and the K_x in the liquid (bottom) phase increases obviously. When the pressure is higher than 3.5 MPa, the liquid phase separates into two liquid phases, the bottom phase is rich in IL, and the water because of the IL absorbs water and the IL is nearly insoluble in the middle and top phases because of the antisolvent effect of CO$_2$. The middle phase is rich in ethyl acetic, which can be known from the data in Table 1. With further increasing pressure, K_x in the bottom phase keeps almost constant. The reason is that the solubility of CO$_2$ in the bottom phase increases slightly because of poor miscibility between water and CO$_2$.[17] On the other hand, the concentration of CO$_2$ in the middle phase increases considerably with increasing pressure, which induces the increases of K_x in this phase greatly. At the same time, the volume of the middle phase also increases with pressure. Therefore, the total conversion of ethanol increases significantly with pressure. As the pressure is higher than about 9.5 MPa, the reaction system enters the two-phase region again. Figure 4 also demonstrates that the effect of pressure on K_x is not considerable in the high-pressure region. This is easy to understand considering the fact that the properties of scCO$_2$ are not sensitive to pressure as pressure is high enough.

The experiments at 9.5 MPa demonstrated that the mole fractions of CO$_2$, ethanol, acetic acid, ethyl acetic, and water in the top phase were 0.791, 0.026, 0.016, 0.139, and 0.028, respectively. We determined the solubility of the IL in the fluid using the apparatus and procedures[18] at this condition using the prepared fluid sample of the same composition, and the value

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was 0.0006 in mole fraction. A high ethanol conversion was obtained for the esterification when the top phase is educed out at the equilibrium conditions. At this condition, a conversion of 86% can be achieved, while the conversion of ethanol without CO_2 determined in this work is only 64%. Thus, CO_2 can be used to improve the conversion of ethanol, and the IL is separated from the desired product (ethyl acetic).

Conclusions

In this work, we studied the effect of compressed CO_2 on the esterification of acetic acid and ethanol in [bmim][HSO_4] at 60.0 °C up to 15 MPa. There was only one phase in the reaction system without CO_2. However, CO_2 can induce phase separation of the reaction system. As the pressure is less than 3.5 MPa, there are two phases in the system and an increase in pressure can enhance the equilibrium conversion. In the pressure range of 3.5−9.5 MPa, there are three phases in the system and the equilibrium conversion increases rapidly with increasing pressure. The third phase disappears as the pressure is larger than 9.5 MPa, and the equilibrium conversion remains at high values and is not sensitive to pressure. Study on the K_x in different phases indicates that the K_x in the middle phase or top phase is much greater than that in the bottom phase. In the presence of CO_2, the total equilibrium conversion can be considerably larger than that in the absence of CO_2. For example, total equilibrium conversion is 64% without CO_2 and can reach 80% as pressure is higher than 9.0 MPa. The idea to induce phase separation and to enhance the reaction efficiency for the reactions in ILs may be applied to some other reactions.

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