Kinetics of Supercritical Fluid Extraction of Ethanol from Aqueous Solution

CLIFFORD Y. TAI AND SHENG-YAN WU

Department of Chemical Engineering, National Taiwan University,
Taipei, Taiwan

A 1.3 dm³ high-pressure vessel was used to extract ethanol from aqueous solution of 10 wt% using supercritical carbon dioxide as a solvent. Experiments were carried out in a semibatch mode. A mathematical model based on the two-film theory was derived for estimating the over all mass transfer coefficient. The effects of operating variables, including pressure, CO₂ superficial velocity, and agitation rate, on the mass transfer coefficient were investigated. In general, the mass transfer coefficient increased with increasing pressure, CO₂ superficial velocity, and agitation rate. The concentration of ethanol recovered in the collector after 180 minutes reached 50 wt%, starting with a feed of 10 wt% ethanol.

Keywords Supercritical fluid extraction; Ethanol; Stirred tank; Mass transfer coefficient

Introduction

Since the energy shortage of the early 1970s, alternatives to energy-intensive separation techniques, such as evaporation and distillation, have been needed for many industrial processes. The recovery of ethanol from a fermented aqueous solution is a typical example. Thus, the extraction of ethanol from water using supercritical fluids has become a popular research topic. A primary goal of such research is to break the ethanol-water azeotrope of 95.5 wt% ethanol. Even if this goal is not achieved, demonstration of a less energy-intensive process to replace conventional distillation for concentrating ethanol is still of interest to the process industry.

In the 1980s, extensive data on the carbon dioxide/ethanol/water system over a wide range of ethanol concentrations, temperatures, and pressures were published. These data were analyzed by McHugh and Krukoni (1986), who showed that the conditions of extraction, i.e., pressure ranging from 975 to 3000 psi and temperature ranging from 20° to 65°C, do not significantly affect the level of extractability achieved. On the other hand, the selectivity of carbon dioxide for ethanol from an ethanol-water mixture is quite high. However, there is an upper limit of the ethanol concentration at around 90 wt%.

One of the advantages of using supercritical carbon dioxide (SC CO₂) as an extraction solvent lies in its mass transport properties. Supercritical carbon dioxide has a liquid-like density, which results in a high level of solubility compared with that of a gas, and a gas-like viscosity, which usually results in a high mass transfer

Address correspondence to Clifford Y. Tai, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106. E-mail: cytai@ntu.edu.tw

coefficient compared with that of a liquid. In addition, the diffusivity of solute in supercritical fluids is generally higher than that in liquids. Therefore, supercritical carbon dioxide seems to be an ideal solvent for extraction. Furthermore, the non toxicity of carbon dioxide makes it a perfect solvent for the extraction of ethanol from alcoholic beverages in order to obtain low-alcohol drinks. For this purpose, liquid membrane (Etuk and Murray, 1990) and gas stripping techniques (Liu and Hsu, 1990) have been studied.

In spite of the advantages of this promising technology, there have been few studies on the mass transfer of supercritical systems. Only a few experiments were performed using a packed bed (Tan et al., 1988; Puiggené et al., 1997; Bernard et al., 1991; Riha and Brunner, 2000). Recently, Tai et al. (2000) studied the extraction kinetics of zinc ion using supercritical CO_2 in a stirred tank. A similar study may be of interest to the chemical industry. For example, ethanol fermentation may be performed in a stirred tank reactor, and in situ ethanol extraction using SC CO_2 may reduce the ethanol toxicity to microorganisms and the cost of purification. For design purposes, this research investigated the effects of operating variables on the mass transfer rate of supercritical CO_2 extraction performed in a 1.3 dm^3 stirred vessel.

Kinetic Model for Estimating the Mass-Transfer Coefficient

The mass transfer between phases in the extraction process of ethanol from water conducted in a stirred vessel is shown in Figure 1. The operation was performed in a semibatch mode; i.e., the aqueous ethanol solution was charged at the beginning of an experiment, while supercritical CO_2 flowed continuously throughout a run.

Figure 1. Mass transfer based on the two-film theory for ethanol extraction in a stirred vessel.

When an impeller was used to agitate the fluids, coarse droplets of SC CO₂, which could be seen through the view port of the extraction vessel, were suspended in the aqueous phase, thus increasing the interfacial area for mass transfer and the extraction efficiency. Since the SC CO₂ was purged continuously, the ethanol concentration of the supercritical phase increased slowly, and the depletion rate of ethanol in the water phase was not high, the two-film theory model was roughly applied. Although the real transport process is more complicated, the simplified model provided a quick way to estimate the mass transfer coefficient and identify important operating variables. In fact, the two-film theory was previously used to interpret mercury extraction kinetics (Larson and Wiencek, 1993) and zinc extraction kinetics (Tai et al., 2000) in a stirred tank.

Assuming that the two-film theory is applied, the mass balance of ethanol in supercritical phase can be written as

$$V_s \frac{dC_s}{dt} = -GC_s + V_l K_s a (C_s^* - C_s) \quad (1)$$

$$= -GC_s + V_l K_s a (mC_l - C_s) \quad (2)$$

where $C_s^* (=mC_l)$ is the concentration of the supercritical phase that would be in equilibrium with the liquid phase concentration, and $K_s a$ is the mass transfer coefficient. The values of m were determined in this experiment at 50°C, and were 0.1778, 0.1610, and 0.1251 for the pressures of 15.3, 13.6, and 10.2 MPa, respectively. The above equation has the following initial condition:

$$C_s = 0 \text{ at } t = 0 \quad (3)$$

On the other hand, the mass balance of ethanol in the liquid phase is

$$\frac{dC_l}{dt} = -K_s a (mC_l - C_s) \quad (4)$$

with the following initial concentration:

$$C_l = C_{l0} \text{ at } t = 0 \quad (5)$$

The above equations can be solved using the Laplace transform method. Let s be the Laplace variable; Equations (2) and (4) are transformed into the following equations:

$$V_s s C_s(s) = -GC_s(s) + V_l K_s a [mC_l(s) - C_s(s)] \quad (6)$$

and

$$sC_l(s) - C_{l0} = -K_s a [mC_l(s) - C_s(s)] \quad (7)$$

Rearranging Equation (6), we have

$$C_s(s) = \frac{V_l K_s a m C_l}{V_s s + G + V_l K_s a} \quad (8)$$

Then Equation (8) can be substituted into Equation (7) to obtain

$$C_l(s) = \frac{(s + A)C_{l0}}{s^2 + q_1 s + q_2} \quad (9)$$

where

$$A = \frac{G}{V_s} + \frac{V_l}{V_s} K_s a \quad (10)$$

$$q_1 = K_s a m + \frac{G}{V_s} + \frac{V_l}{V_s} K_s a \quad (11)$$

$$q_2 = K_s a m G / V_s \quad (12)$$

Therefore,

$$C_l = C_{l0} [\beta_1 \exp(\alpha_1 t) + \beta_2 \exp(\alpha_2 t)] \quad (13)$$

where

$$\beta_1 = \frac{\alpha_1 + A}{\alpha_1 - \alpha_2} \quad (14)$$

$$\beta_2 = \frac{\alpha_2 + A}{\alpha_2 - \alpha_1} \quad (15)$$

$$\alpha_1 = \frac{-q_1 + \sqrt{q_1^2 - 4q_2}}{2} \quad (16)$$

$$\alpha_2 = \frac{-q_1 - \sqrt{q_1^2 - 4q_2}}{2} \quad (17)$$

Figure 2. Flow diagram of the ethanol extraction process: 1. CO₂ cylinder, 2. filter, 3. refrigerator, 4. mini pump, 5. preheater, 6. heater, 7. check value, 8. extractor, 9. voltage controller, 10. voltage controller, 11. coil, 12. sampling valve, 13. heating tape, 14. view port, 15. pressure gauge, 16. paddle, 17. temperature indicator, 18. safety valve, 19. tachometer, 20. motor, 21. ball valve, 22. metering valve, 23. cold trap, 24. collector, 25. rotameter, 26. dry test meter.

Since α_1 and α_2 are smaller than zero, and since $\alpha_1 > \alpha_2$, the value of $\exp(\alpha_1 t)$ will be much greater than that of $\exp(\alpha_2 t)$ after a certain period of operation. Thus, Equation (13) can be reduced to

$$C_l = C_{l0} \beta_1 \exp(\alpha_1 t) \quad (18)$$

From Equation (18), we know that α_1 is the slope of a straight line when we plot $\ln C_l$ versus t .

Since m , V_l , G , and V_s are known, the mass transfer coefficient can be calculated using the following equation, which is obtained by rearranging Equation (16):

$$K_s a = - \frac{\alpha_1 (1 + \alpha_1 V_s / G)}{m[(\alpha_1 V_s / G) + 1] + \alpha_1 V_l / G} \quad (19)$$

Experimental Section

Extraction experiments were performed in a 1.3 dm³ semibatch extractor. The flow diagram of the experimental setup is shown in Figure 2, which is essentially the same as that used by Tai et al. (2000, 2001). The system was mainly composed of three parts: (1) a feeding system, (2) a pressurized extractor with temperature control,

Figure 3. Ethanol concentration profile of liquid phase for run number 12. Operating conditions: temperature, 50°C; superficial velocity, 1.25×10^{-4} m/s; agitation rate, 8.3 Hz; pressure, 13.6 MPa.

and (3) a CO₂ feed rate measurement system. The feeding system consisted of a CO₂ cylinder, a cooler for preventing liquid CO₂ from vaporizing, a piston pump (Milton Roy) for feeding liquid CO₂, and a preheater. The extraction vessel was equipped with an agitator, a coil, a pair of viewing windows, and a sampling valve (Rheodyne, model 7010), and it was wrapped with heating tape for the purpose of temperature control. The measuring system consisted of a metering valve for controlling the depressurization rate and a dry test meter for measuring the CO₂ flow rate. The metering valve had to be heated; otherwise, clogging could occur due to the solidification of CO₂ during depressurization.

At the beginning of an experimental run, a volume of 0.8 dm³ aqueous solution of 10 wt% ethanol was charged into the extractor. Then, CO₂ (industrial grade with a purity of 99.5%, containing 0.25 molar ppm H₂O) was pumped into the vessel until the vessel pressure reached the desired value. At this moment, the outlet valves were opened and the metering valve was adjusted to keep the vessel pressure constant; then, agitation was started. The volume hold up of SC CO₂ was about 38% of the extractor volume. The SC CO₂ was then passed through the metering valve to reduce its pressure and flow and through a cold trap to remove ethanol and water. Then, the dry test meter recorded the amount of CO₂. A liquid sample of 5 mL was removed from the extractor once every 30 minutes, and the concentration of the solution was analyzed with a gas chromatograph (Shimadzu, model GC-14A), using Porapak Q packing material and a flame ionization detector (FID).

Figure 4. Logarithmic plot of Equation (18) for run number 12.

Results and Discussion

In this study, experiments on extracting ethanol from aqueous solution were performed at 50°C under different CO₂ flow rates, agitation rates, and system pressures. A temperature of 50°C was chosen because the mass transfer rate was previously found to increase with temperature (Brunner and Kreim, 1986), and because 50°C was about the highest temperature we could obtain in our system. Experimental data reported in this study are the average of two runs and are within a 10% difference.

Determination of the Mass Transfer Coefficient

A typical concentration profile of ethanol in aqueous phase is shown in Figure 3, in which the ethanol concentration decreases with time. According to Equation (18), a plot of $\ln C_l$ against t will give a straight line with a slope of α_1 . Such a plot is shown in Figure 4, with a correlation coefficient of 0.98. Then, after α_1 is substituted into Equation (19), the mass transfer coefficient, $K_s a$, can be determined. Once the value of $K_s a$ is available, it can be used to check the assumption that neglects the second term on the right-hand side of Equation (13). $K_s a$ is substituted into Equations (11)

Figure 5. Pressure effect on the extraction rate. Operating conditions: temperature, 50°C; superficial velocity, 1.25×10^{-4} m/s; agitation rate, 8.3 Hz.

and (12) to calculate q_1 and q_2 , and then α_1 and α_2 are determined as follows: $\alpha_1 = -4.09 \times 10^{-5} \text{ s}^{-1}$ and $\alpha_2 = -1.81 \times 10^{-2} \text{ s}^{-1}$. Then the magnitudes of the two terms on the right-hand side of Equation (13) can be compared. For example, $\exp(\alpha_1 t) = 226 \exp(\alpha_2 t)$ at $t = 300 \text{ s}$. Thus, the assumption that neglects $\beta_2 \exp(\alpha_2 t)$ is reasonable.

Effect of Pressure on the Mass Transfer Coefficient

With the operating temperature and CO_2 superficial velocity fixed at 50°C and $1.25 \times 10^{-4} \text{ m/s}$, the pressure effect on the mass transfer rate was investigated at three agitation rates, i.e., 8.3, 11.7, and 15.0 Hz. Figure 5 shows the ethanol concentration profile of the liquid phase when extraction was performed at 10.2, 13.6, and 15.3 MPa under an agitation rate of 8.3 Hz. The extraction rate was higher under higher pressure. Using the technique previously described, the mass transfer coefficients were determined and are plotted in Figure 6. It is clear that the mass transfer coefficient increased with increasing pressure and that the agitation rate was less influential than pressure on the mass transfer rate.

The effect of pressure on the mass transfer rate is a complicated problem. When the pressure increases, the properties of both phases will change. Some changes turn

Figure 6. Pressure effect on the mass transfer coefficient for three agitation rates.

out to be in favor of the mass transfer rate, but others have the opposite effect. Although the system property data of water/ethanol/SC CO₂ are not sufficient to reveal the pressure effect, it is our intention to explain it based on the following arguments.

Mehta and Sharma (1970) investigated the effect of surface tension on the interfacial area in an agitated gas-liquid contactor. They concluded that a system with lower surface tension (carbon dioxide/water/monoethanolamine) possesses a higher interfacial area, i.e., smaller gas bubbles dispersed in the liquid, than does a system with higher surface tension (carbon dioxide/butanol/monoethanolamine). This is consistent with a correlation presented by McCabe et al. (2001), although it was not derived under supercritical conditions. In our system, the solubility of CO₂ in water increased with increasing pressure, thus causing the surface tension to decrease. The lower surface tension resulted in a larger interfacial area due to the formation of smaller bubbles. Therefore, the interfacial area, a , increased with increasing pressure. At higher pressure, on the other hand, the viscosity of the supercritical phase will increase (Stephan and Lucas, 1979), and the diffusivity of ethanol might decrease based on the results obtained for other systems (such as naphthalene and caffeine in supercritical CO₂) (Feist and Scheider, 1982); both will cause K_s to decrease. It is conjectured that the effects of diffusivity and viscosity

Figure 7. Effect of the CO₂ superficial velocity on the extraction rate. Fixed operating conditions: temperature, 50°C; pressure, 15.3 MPa; agitation rate, 8.3 Hz.

are less important than the effect of surface tension. As a result, the mass transfer coefficient, $K_s a$, increases at higher pressures.

Effect of CO₂ Superficial Velocity

The effect of the CO₂ superficial velocity on the extraction rate of ethanol was investigated for three levels of pressure, i.e., 10.2, 13.6, and 15.3 MPa. A typical result shown in Figure 7 for 15.3 MPa indicates that the extraction rate increased with an increase in the CO₂ superficial velocity, defined as (CO₂ volumetric flow rate)/(cross section area of extractor), which varied here from 5.36×10^{-5} to 1.25×10^{-4} m/s. In addition, the estimated mass transfer coefficients are plotted in Figure 8. The mass transfer coefficient increased with an increase in the CO₂ superficial velocity for all three levels of pressure. These findings can be explained by using the results reported by Oyevaar et al. (1991), assuming that the increase in the mass transfer coefficient is due to an increase in the interfacial area between the SC CO₂ bubbles and the aqueous phase. They investigated the CO₂ superficial velocity and pressure effects on the interfacial area in a mechanically agitated gas-liquid contactor operated at pressures up to 8.0 MPa. A positive influence of pressure on the interfacial area was observed for higher CO₂ superficial velocity and higher pressure.

Figure 8. Effect of the superficial velocity on the mass transfer coefficient for various pressures. Fixed operating conditions: temperature, 50°C; agitation rate, 8.3 Hz.

Effect of Agitation Rate

Three agitation rates were tested to determine the effect of agitation on the mass transfer coefficient. In Figure 9, the mass transfer coefficient is plotted against the agitation rate at various CO₂ superficial velocities. The mass transfer coefficient increased with increasing agitation rate; however, the agitation rate had no effect at the highest CO₂ velocity, 1.25×10^{-4} m/s. This phenomenon can be explained using the concept of the minimum agitation rate proposed by Westerterp et al. (1963), i.e., the impeller tip velocity must exceed the gas rising velocity a certain number of times in order for all the big gas bubbles to be broken up into small bubbles. Using a chemical reaction method to estimate the interfacial area created by an impeller in a gas-liquid contactor, they found that the interfacial area increased as the agitation rate increased and was not influenced by the gas flow rate when the agitation rate was higher than the minimum agitation rate. On the other hand, the interfacial area remained constant when the agitation rate was lower than the minimum agitation rate. Since the minimum agitation rate increased as CO₂ flow rate increased, the agitation rates studied in our experiment may have been below the minimum value for the highest CO₂ superficial velocity, 1.25×10^{-4} m/s. The interfacial area and, thus, the mass transfer coefficient remained constant. For the lowest superficial velocity, 5.36×10^{-5} m/s, the agitation rate, 8.3 Hz, exceeded the

Figure 9. Effect of the agitation rate on the mass transfer coefficient for various CO₂ superficial velocities. Other operating conditions: temperature, 50°C; pressure, 15.3 MPa.

Figure 10. Concentration of ethanol recovered in the collector.

minimum value, thus, the interfacial area or mass transfer coefficient increased as the agitation rate increased.

Concentration of Recovered Ethanol

The starting materials for this experiment contained 10 wt% ethanol. Under various operating conditions, the concentration of ethanol recovered from the collector after 180 minutes of operation reached 50 wt%. Typical results are shown in Figure 10 for the two CO₂ superficial velocities. The general trend observed in the figure indicates that the higher the pressure and velocity, the higher the concentration of recovered ethanol. The recovered concentration of ethanol was always less than the theoretical value estimated from equilibrium concentration, which is higher than 90 wt% (McHugh and Krukonis, 1986). It is assumed that the supercritical CO₂ phase did not reach equilibrium or that perhaps some of the extracted ethanol was carried out of the collector by the depressurized CO₂ gas and lost to the atmosphere.

Conclusions

With a starting material of 10 wt% aqueous solution, when supercritical CO₂ was used as a solvent for extracting ethanol from an aqueous solution in a stirred vessel operated in a semibatch mode, the concentration of recovered ethanol reached

50 wt%. The mass transfer coefficient of the extraction process increased with increasing pressure, CO₂ superficial velocity, and agitation rate. The increase in the extraction rate was mainly due to an increase in the interfacial area between the SC CO₂ bubbles and the aqueous phase.

Acknowledgment

The authors gratefully acknowledge the financial support provided by the National Science Council of the Republic of China.

Nomenclature

A	$G/V_s + (V_l/V_s)K_s a$ as defined in Equation (10), 1/s
a	interfacial area, m ² /m ³
C_l	concentration of ethanol in liquid phase, k mol/m ³
C_{li}	interfacial concentration of ethanol in liquid phase, k mol/m ³
C_{l0}	initial concentration of ethanol in liquid phase, k mol/m ³
$C_l(s)$	transformed C_l , s·k mol/m ³
C_r	ethanol concentration recovered in the collector, wt%
C_s	concentration of ethanol in SC CO ₂ phase, k mol/m ³
C_{si}	interfacial concentration of ethanol in supercritical phase, k mol/m ³
$C_s^*(s)$	transformed C_s , s·k mol/m ³
C_s^*	mC_l , ethanol concentration of supercritical phase in equilibrium with the liquid phase concentration, k mol/m ³
G	volumetric flow rate of SC CO ₂ , m ³ /s
$K_s a$	overall mass transfer coefficient, 1/s
m	equilibrium constant
N	mixing rate, Hz
P	pressure, MPa
q_1	$K_s a m + G/V_s + (V_l/V_s)K_s a$ as defined in Equation (11), 1/s
q_2	$K_s a m (G/V_s)$ as defined in Equation (12), 1/s ²
s	Laplace variable, 1/s
t	time, s
U_s	superficial velocity of SC CO ₂ , m/s
V_l	volume of liquid phase in the extractor, m ³
V_s	volume of SC CO ₂ in the extractor, m ³
α_1	$= (-q_1 + \sqrt{q_1^2 - 4q_2})/2$ as defined in Equation (16), 1/s
α_2	$= (-q_1 - \sqrt{q_1^2 - 4q_2})/2$ as defined in Equation (17), 1/s
β_1	$= (\alpha_1 + A)/(\alpha_1 - \alpha_2)$, dimensionless
β_2	$= (\alpha_2 + A)/(\alpha_2 - \alpha_1)$, dimensionless

References

- Bernard, L., Keller, A., Barth, D., and Perrut, M. (1991). Separation of ethanol from aqueous solutions by supercritical carbon dioxide: Comparison between simulations and experiments, in *Proceedings of the 2nd International Symposium on Supercritical Fluids*, 394–397, Boston.

- Brunner, G. and Kreim, K. (1986). *Ger. Chem. Eng.*, **9**, 246.
- Etuk, B. R. and Murray, K. R. (1990). *I. Chem. E. Symp. Ser.*, **119**, 279.
- Feist, R. and Schneider, G. M. (1982). *Sep. Sci. Technol.*, **17**, 261.
- Larson, K. and Wiencek, J. M. (1993). *Ind. Eng. Chem. Res.*, **32**, 2854.
- Liu, H.-S. and Hsu, H.-W. (1990). *Chem. Eng. Sci.*, **45**, 1289.
- McCabe, W. L., Smith, J. C., and Harriot, P. (2001). Unit Operations of Chemical Engineering, 6th ed., chap. 9, 238–285, McGraw-Hill, Taipei, Taiwan.
- McHugh, M. and Krukons, V. (1986). Supercritical Fluid Extraction: Principles and Practice, chap. 8, 117–142, Butterworths, Boston.
- Mehta, V. D. and Sharma, M. M. (1970). *Chem. Eng. Sci.*, **26**, 461.
- Oyevaar, M. H., Bos, R., and Westerterp, K. R. (1991). *Chem. Eng. Sci.*, **46**, 1217.
- Puiggené, J., Larrayoz, M. A., and Recasens, F. (1997). *Chem. Eng. Sci.*, **52**, 195.
- Riha, V. and Brunner, G. (2000). *J. Supercrit. Fluids*, **17**, 55.
- Stephan, K. and Lucas, K. (1979). Viscosity of Dense Fluids, 75–79, Plenum, New York.
- Tai, C. Y., You, G.-S., and Chen, S.-L. (2000). *J. Supercrit. Fluids*, **18**, 201.
- Tai, C. Y., Huang, S.-C., Huang, M.-S., and Liu, H.-S. (2001). *J. Chin. Inst. Chem. Eng.*, **32**, 269.
- Tan, C. S., Liang, S. K., and Liou, D. C. (1988). *Chem. Eng. J.*, **38**, 17.
- Westerterp, K. R., van Dierendonck, L. L., and de Kraa, J. A. (1963). *Chem. Eng. Sci.*, **18**, 157.

Copyright of Chemical Engineering Communications is the property of Taylor & Francis Ltd. The copyright in an individual article may be maintained by the author in certain cases. Content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.