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This study examined the use of ethyl acetate and its mixture with ethanol as cosolvent for the extraction of biologically derived 1,3-propanediol (1,3-PDO) from a fermentional process. Experimental results on extraction of the fermentation model mixture revealed that ethyl acetate was a suitable solvent, having the distribution coefficient of 1,3-PDO of 0.22 at 303.15 K. The temperature (303.15 to 323.15 K) was found not to have a significant effect on the distribution coefficient. On the other hand, the addition of glycerol into the feed aqueous stream (at the concentrations of 4, 8, 12 g/L) was found to increase the distribution coefficient of 1,3-PDOs, however, the compound selectivity decreased. When ethanol was used as a cosolvent at the volume ratio of ethyl acetate to ethanol of 90:10, the distribution coefficient increased from 0.22 to 0.31 at 303.15 K. This decreased the number of theoretical stages (NTS) required to achieve 90% recovery of 1,3-PDO from the aqueous phase from 3 to 2 stages at the solvent to feed (S/F) ratio of 9. In addition, the extraction results with actual fermentation broth at 303.15 K indicated that the use of ethanol cosolvent could improve the distribution coefficient of 1,3 PDO from 0.14 to 0.20.

Keywords cosolvent; *Costridium butyricum*; fermentation; liquid-liquid extraction; 1,3 propanediol

INTRODUCTION

For decades, 1,3-Propanediol (1,3-PDO) has been one of the major monomer components for the production of high performance polyester such as polytrimethylene terephthalate (PTT). The PTT produced from 1,3-PDO has excellent physical properties and is suitable for fiber and textile applications. Nowadays, 1,3-PDO can be produced either by a chemical method or a biotechnological method. In the chemical method, 1,3-PDO is obtained by hydration of acrolein and hydroformylation reaction of ethylene oxide. However, the process becomes less important nowadays as the prices of petroleum derived raw materials required for chemical process tend to increase continuously. Moreover, the process involves the use of toxic chemicals and their emissions are of high environmental concerns. On the other hand, 1,3-PDO can be produced by the biotechnological method through the conversion of glycerol to 1,3-PDO using microorganisms such as *Klebsiella pneumoniae, Citrobacter frundii, Enterobacter agglomerans, Clostridium butyricum*. This bioconversion is of increasing interest as a result of the growing volume of glycerol, a by-product in biodiesel production and a minor by-product in ethanol fermentation. Moreover, this method operates at environmentally benign conditions (1).

Despite the advantages of the biological process, the separation and purification of 1,3-PDO from fermentation broth is not straightforward because 1,3-PDO has low volatility and high hydrophilic characteristics in dilute aqueous solutions. Ames (2002) disclosed a process for separation and purification of 1,3-PDO by evaporation and distillation but the requirement for a large amount of energy made this process unprofitable (2). Compared with distillation, solvent extraction requires lower energy consumption. Malinowski (1999) reported the theoretical evaluation of the downstream separation of 1,3-PDO from dilute aqueous solutions by liquid-liquid extraction with aliphatic aldehydes and alcohols and found the distribution of 1,3-PDO into aldehydes and alcohols appeared to be low (3). Alternatively, Malinowski (2000) developed the 1,3-PDO purification process based on the reactive extraction, using aldehydes as a reactant to first convert 1,3-PDO to alkyl dioxane, which was then extracted with an organic solvent such as toluene, o-xylene, and ethylbenzene (4). Yan et al. (2005) later proposed a similar but improved reactive extraction process using aldehydes as both the reactant and the extraction solvent (5). Although a high extraction yield was resulted, the process involves several

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steps as the dioxane product needs to be converted back to 1,3-PDO by hydrolysis. Furthermore, the separation of 1,3-PDO from the mixture of 1,3-PDO and aldehyde is then required, making reactive extraction too complicated to achieve a satisfactory result. Alternatively, Li et al. (2001) applied pervaporation using a ZSM-5 zeolite membrane for the separation of 1,3-PDO from glycerol and glucose in aqueous solutions; however, this method has some drawbacks such as low flux and low selectivity (6). Roturier et al. (2002) and Hilaly et al. (2002) used the chromatographic column packed with cation exchange resin for the recovery of 1,3-propanediol. This method consumed less energy and satisfied the environmental protection standards, however, it was difficult to obtain 1,3-PDO with high purity and the process required the dewatering step (7,8). Corbin et al. (2003) suggested the separation of 1,3-PDO, glycerol, and a mixture of 1,3-PDO and glycerol from a biological mixture could be achieved with the yield greater than 90% using several types of molecular sieve (9). However, the mixture must still be purified further using conventional separation methods such as distillation.

Recently, Cho et al. (2006) developed a novel isolation and purification method for producing 1,3-PDO with high purity and high yield (10). This method employed solvent extraction with ethyl acetate to concentrate 1,3-PDO from fermentation broth and the extract was purified through silica gel chromatography column to separate 1,3-PDO from the mixture of 1,3-PDO and 1,2-PDO. The author suggested that the solvent extraction process proposed was simple and efficient for the isolation of 1,3-PDO from the other components in the fermentation mixture. However, the results presented in such a study focused on the steps of chromatography rather than the solvent extraction process. Therefore, in this work, we proposed to investigate the extraction of 1,3-PDO with ethyl acetate from fermentation process using synthetic broth. First, liquid-liquid equilibrium data were measured experimentally at a temperature of 303.15 K in order to evaluate process performance. The tie line data were correlated using the methods proposed by Othmer-Tobias and Hand (11).

Furthermore the effect of temperature and the presence of glycerol at different concentration, and the use of ethanol as cosolvent were investigated on the extraction process and the number of theoretical stages was determined. Finally, the extraction process was experimentally tested using actual fermentation broth.

MATERIALS AND METHODS

Chemicals

The model mixture used in this study was 1,3-PDO and glycerol in aqueous solution. 1,3-PDO (98% purity) was purchased from Acros Organic Co. Glycerol (99.5% purity) was supplied from Ajax Finechem. Ethyl acetate used for extraction was analytical grade, and was obtained from Fisher Scientific, UK. Ethanol (99.7% purity) was supplied from VWR International Ltd., UK.

Experimental Determination of Equilibrium Data

Determination of Binodal Curve

The determination of binodal curve data was conducted at isothermal condition in a 100 mL equilibrium cell equipped with a magnetic stirrer. The cell was charged with homogeneous aqeous1,3-PDO mixtures. Then the solvent was added slowly into the cell until the end point was reached, as indicated by the onset of permanent turbidity (12).

Determination of Tie Lines

The tie lines data were experimentally obtained at a controlled temperature by mixing 20 mL of the organic solvent and 20 mL of an aqueous solution of 1,3-PDO in the equilibrium cell with the stirring rate of 150 rpm until the system reached equilibrium (approximately 40 min). In this experiment, the temperature was controlled by means of a water bath, and the aqueous mixtures of 1,3-PDO were prepared at five different concentrations. The mixture was then centrifuged for 30 min at 30°C and 500 rpm to obtain complete phase separation. The organic phase and the aqueous phase were separated and the volumes were measured. The remaining solvent in the aqueous phase was then evaporated using a vacuum rotary evaporator at 35°C for 10 min. The aqueous phase was then analyzed with an HPLC analytical column. This procedure allows for the determination of partition coefficients of 1,3-PDO between the organic phase and the aqueous phase. The effects of temperatures, the presence of glycerol, and the addition of ethanol as a cosolvent on the extraction coefficient were determined at various experimental conditions as summarized in Table 1.

Extraction of 1,3-PDO from Actual Fermentation Broth

Extraction of 1,3-PDO with selected solvent systems (ethyl acetate and ethylacetae:ethanol mixture at the volume ratio of 90:10) was evaluated at 303.15 K using actual fermentation broth. The fermentation broth used

TABLE 1
Experimental variables for extraction of 1,3-PDO

Experimental variables	Ranges
Temperature (K)	303.15, 313.15, 323.15
Glycerol in feed mixture mass ratios (g glycerol: g 1,3-PDO)	12:60, 8:60, 4:60
Ethanol cosolvent concentration in 1,3-PDO (mL ethyl acetate:mL ethanol)	95:5, 90:10

in this experiment was derived from glycerol fermentation by *C. butyricum* DSM 5431 cultivated under an anaerobic condition at 33°C and pH 7. The initial concentration of glycerol in the feed was 100 g/L and the final concentration of 1,3-PDO and glycerol were 38.6 g/L and 7.4 g/L, respectively.

Analysis

Chemical Analysis

A High performance lquid chromatography (HPLC, Lichrocart-C18) system was used to measure the concentration of 1,3-PDO and glycerol in the aqueous (raffinate) phase. Lichrocart-C18 column (250 mm × 4 mm I.D.) was used as an HPLC analytical column. The isocratic system of 5% v/v of methanol in water (pH = 6.5) was employed as a mobile phase at room temperature. The flow rate of the mobile phase was maintained at 0.5 ml/min and an injection volume of 20 μL was used. The column effluent was monitored with a refractive index detector. The 1, 3-PDO standard calibration curve was prepared by plotting the concentrations versus the peak areas for the aqueous solutions of 1,3-PDO in the range of the concentrations between 0–80 g/L. The variation coefficient here was found to be 0.99.

Data Analysis

From the experimental data, the mass fractions of the solute in the aqueous phase and that in the extract phase could be determined. In this work, the reliability of experimentally measured tie-line data was determined using Othmer and Tobias (Eq. 1) and Hand (Eq. 2) correlation. The linearity of the plots indicates the degree of consistency of the related data (11).

$$\ln\left(\frac{(1-W_{33})}{W_{33}}\right) = a_1 + b_1 \ln\left(\frac{(1-W_{11})}{W_{11}}\right) \quad (1)$$

$$\ln\left(\frac{W_{23}}{W_{33}}\right) = a_2 + b_2 \ln\left(\frac{W_{21}}{W_{11}}\right) \quad (2)$$

in which $W_{i,j}$(i, j = 1, 2, 3) in the above equations represent the mass fraction of species i in species j. The subscripts 1, 2, and 3 represent water, 1,3-PDO, and ethyl acetate, respectively.

The distribution coefficient of a solute i (1,3-PDO or glycerol), $K_{D,i}$, was calculated based on its definition as the ratio of the determined solute mass fraction in the organic phase, $W_{i,3}$, and that in the aqueous phase, $W_{i,2}$, at equilibrium:

$$K_{D,i} = \frac{W_{i,3}}{W_{i,2}} \quad (3)$$

In case of extraction with the addition of glycerol to the feed, the selectivity was determined from the distribution coefficient of 1,3-PDO divided by the distribution coefficient of glycerol.

RESULTS AND DISCUSSION

Experimental Equilibrium and Data Correlation

To evaluate the suitable solvent that possesses a favorable interaction with 1,3-PDO, experimental liquid-liquid equilibrium data were determined for water-1,3-PDO-ethyl acetate ternary mixtures at a temperature of 303.15 K. The experimental data were plotted on a ternary diagram in Fig. 1, which shows the binodal curve, representing the boundary line between the liquid single-phase region and the two phase area. The lines connecting the two points are called tie lines. In general extraction operation, the solvent should have a large two-phase area, with a minimum mutual solubility and distribution in favor of the solvent. According to Fig. 1, the tie lines show the distribution of 1,3-PDO at equilibrium is in favor of the aqueous phase. The results show a similar behavior to the prediction using UNIFAC equation. Nevertheless, the experimental mutual solubility of 1,3-PDO from the extraction with ethyl acetate was smaller than the calculated mutual solubility due to the slightly larger two-phase area of the ternary system as shown in the figure. The dashed line represented the binodal line obtained theoretically using the UNIFAC model. Because, in the calculation of the phase equilibrium data using the UNIFAC model, liquid-phase activity coefficients were related to the interactions between their functional groups, instead of the interaction between the molecules, the calculated data using the UNIFAC equation therefore gave a large deviation from the experimental phase equilibrium data.

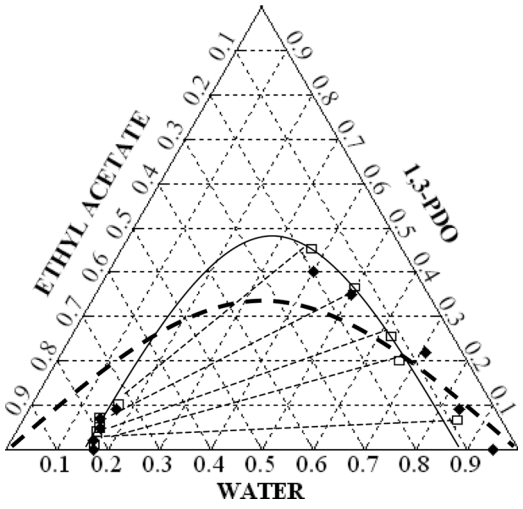

FIG. 1. Liquid-liquid equilibrium data for ternary system of 1,3-PDO-water-ethyl acetate at 303.15 K: (–) calculated data from UNIFAC model at 303.15 K; (◆) experimental binodal curve data, (□) experimental tie line data.

The Othmer and Tobias plot and the Hand plot are shown in Fig. 2 (a and b). In this study, the correlation coefficient (R^2) for the Othmer-Tobias and Hand are 0.9428 and 0.9904, respectively; therefore, these data are sufficient for the determination of the tie line compositions.

The distribution coefficient of the extraction system could be determined from the mass fractions of 1,3-PDO in the solvent phase, W_{23}, and that in the aqueous phase, W_{21}, at equilibrium, respectively, as shown in Fig. 3. For extraction with ethyl acetate, the distribution coefficient of 1,3-PDO at 303.15 K was found to be in favor of the aqueous phase and the distribution coefficient determined from the slope of the linear regression of the plot in Fig. 3 was 0.22. This value was comparable to that from previous literature, in which tributyl phosphate was used for extraction of 1,3-PDO from the aqueous solution and its distribution coefficient was reported to be 0.203 (13). Although, the mutual solubility of 1,3-PDO and tributyl phosphate is lower than the mutual solubility of 1,3-PDO and ethyl acetate due to the higher hydrophobic parameter, tributyl phosphate is more difficult to separate from the extract phase due to its high boiling point. On the other hand, ethyl acetate can be easily separated from the extract phase since the boiling point of ethyl acetate is low. From these results, we can conclude that ethyl acetate is a potential alternative solvent for the extraction of 1,3-PDO from the aqueous solution.

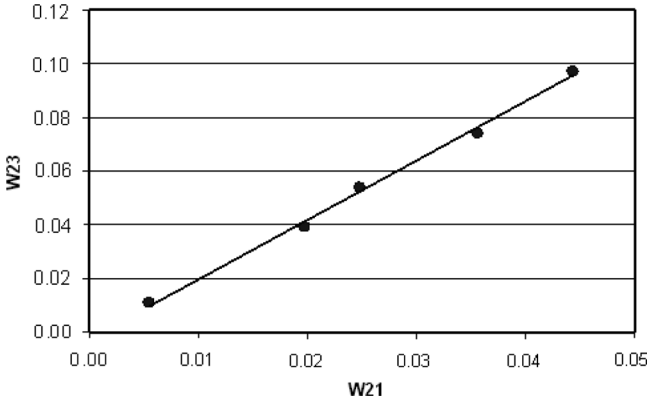

FIG. 3. Equilibrium mass fraction of 1,3-PDO (2) in ethyl acetate (3) versus mass fraction of 1,3-PDO (2) in Water (1) at 303.15 K.

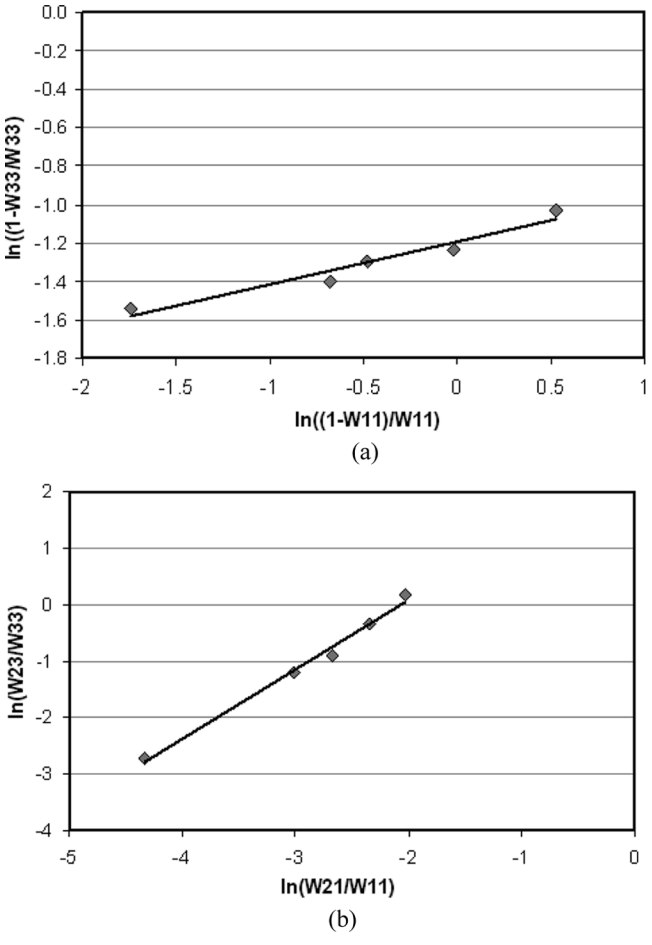

FIG. 2. (a) Othmer and Tobias plot for the water (1)-1,3-PDO (2)-ethyl acetate (3) system at 303.15 K (b) Hand plot for the water (1)-1,3-PDO (2)-ethyl acetate (3) system at 303.15 K.

Number of Theoretical Stages

The number of theoretical stages required to achieved 90% recovery of of 1,3-PDO from aqueous solutions, NTS(90%), for extraction with ethyl acetate was calculated. Using a graphical method, the data for equilibrium composition and tie line data were used for calculating the minimum solvent to feed ratio, $(S/F)_{min}$, which was determined to be $(S/F)_{min} = 2.03$. Generally, the actual solvent-to-feed ratio for an extraction system should be 1.5 times $(S/F)_{min}$ (14), or 3.05 for 1,3-PDO extraction with ethyl acetate in this work. Assuming low concentration of glycerol in the aqueous solution, the mutual solubility of the solvent remained nearly constant, and a constant flow rates of feed and extraction solvent streams, the mass fraction of 1,3-PDO in the raffinate phase after extraction was calculated and the results are shown in Fig. 4 as a function of the number of equilibrium stages for the S/F ratio of 3.05, 5 and 9. The solid lines shown in this figure were determined from $K = 0.22$, which indicated that the amount of 1,3-PDO extracted increased when the number of stages increases, and that the number of stages could be decreased by increasing S/F ratio. It can be seen from this figure that the maximum 1,3-PDO recovery of only 68% could be achieved with the S/F ratio of 3.05, indicating that higher S/F ratios would be required for the extraction of 1,3-PDO with ethyl acetate from the aqueous system of solution. To validate this prediction, an experiment was carried out for extraction with ethyl acetate at

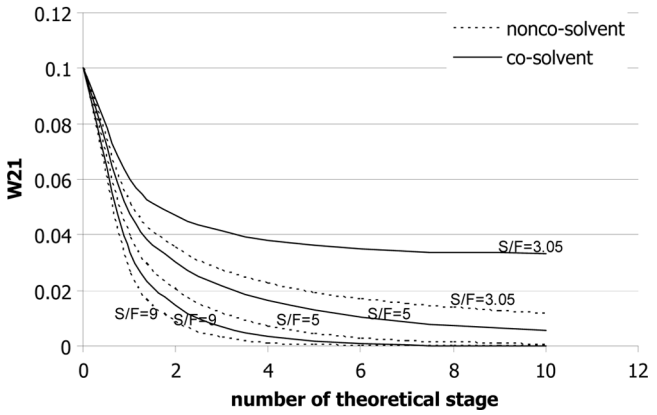

FIG. 4. 1,3-PDO raffinate mass fraction at 303.15 K as function of NTS.

303.15 K with S/F ratio = 9, and it was found that the recovery of 90% could be achieved in 5 stages (calculated NTS (90%) = 3). Although the experimental results require larger number of stages than theoretical prediction, it reasonably proves the feasibility of using the solvent for extraction of 1,3-PDO from the biologically derived aqueous system of solution. The process could further be improved by a better design of the system of extraction to ensure that equilibrium conditions be reached at each stage of extraction.

Effect of Temperature on 1,3-PDO Extraction

The effect of temperature on the distribution of 1,3-PDO was determined for the system of 1,3-PDO, water, and ethyl acetate (in absence of glycerol). Here, the extraction experiments were carried out at various temperatures: 303.15 K, 313.15 K, and 323.15 K. The experimental distribution coefficients are summarized in Table 2. When the temperature increases, the partition coefficients of 1,3-PDO decreases slightly. With these results, the required number of theoretical stages to achieve 90% recovery, NTS (90%), determined for S/F ratio = 5 was found to increase considerably. Therefore from this result, the extraction temperature at 303.15 K is the most suitable for extraction of 1,3-PDO from aqueous solution.

TABLE 2
Effect of temperature on partition coefficient of 1,3-PDO and calculated NTS (90%) at different S/F ratio = 3.50 and 5

Temperature (K)	$K_{1,3\text{-PDO}}$	NTS (90%) S/F = 3.05	NTS (90%) S/F = 5
303.15	0.22	–	7
313.15	0.19	–	12
323.15	0.19	–	17

Effect of Residual Glycerol on 1,3-PDO Extraction

Generally, in a batch culture, glycerol is almost completely consumed at low initial glycerol concentration (15). In continuous culture on the other hand, the culture presented high dilution rates, causing the amounts of residual glycerol in the fermentation broth to increase (16). For this reason, it is important to investigate the effect of residual glycerol from fermentation. In this study, we investigated the effect of residual glycerol in three mass fractions: the mass ratio of 60 g 1,3-PDO to 12 g glycerol, 60 g 1,3-PDO to 8 g glycerol, and 60 g 1,3-PDO to 4 g glycerol in 1 L solution. These ratios lie within the typical range of concentration of residual glycerol in fermentation broth base on literature data (17). From these results, the distribution coefficient of 1,3-PDO and glycerol, as well as the selectivity were calculated as summarized in Table 3.

As seen in Table 3, the distribution of 1,3-PDO increased in favor of the solvent phase when the amounts of glycerol added to the feed increased. On the other hand, the selectivity was found to decrease with increasing glycerol concentration. The distribution coefficient of 1,3-PDO was slightly increased at low concentration of glycerol and was increased to 0.28 at high concentration of glycerol. Due to the polarity and hydrogen bonding characteristics of glycerol, the increased amount of residual glycerol results in the intermolecular interactions between water and 1,3-PDO. The glycerol molecules are highly polar molecules and bind water more strongly than 1,3-PDO, thus the molecular interactions between water and 1,3-PDO tend to decrease.

Based on these results, the NTS (90%) in the case of glycerol addition was found to decrease for small S/F ratio but the value was not significantly different from extraction 1,3-PDO without glycerol addition at higher S/F ratio. However, the selectivity for 1,3-PDO was decreased considerably in the presence of glycerol. It was therefore recommended that glycerol concentration in the aqueous phase should be kept at minimum.

Extraction of 1,3-PDO with Ethanol Cosolvent

In this study, the effect of adding ethyl alcohol as cosolvent was investigated for the extraction of 1,3-PDO from the model aqueous solutions (60 g/L), without glycerol. The results shown in Fig. 5 indicated that the distribution coefficient of 1,3-PDO increased as the volume fraction of ethanol increased. For extraction with ethyl acetate:ethanol mixture at 90:10 volume ration, the distribution coefficient of 1,3-PDO increased approximately 40%, compared with the extraction with ethyl acetate alone (from 0.22 to 0.31). This increase was due to the increase in mixture polarity as the volume fraction of ethanol in ethyl acetate increased. However, the loss of solvent into the raffinate phase increased when the fraction of ethanol in the solvent stream increased.

TABLE 3
Calculated distribution coefficients of 1,3-PDO and glycerol at 303.15 K and NTS (90%) at various S/F ratios

1,3-PDO: glycerol(g/g) in 1 L feed	$K_{1,3\text{-PDO}}$	NTS(*90%)							K_{gly}	Selectivity ($K_{1,3\text{-PDO}}/K_{gly}$)
		S/F = 3.05	S/F = 5	S/F = 6	S/F = 7	S/F = 8	S/F = 9	S/F = 10		
60:0	0.22	–	7	5	4	3	3	3	–	–
60:4	0.23	–	6	4	4	3	3	3	0.08	2.9
60:8	0.25	–	5	4	3	3	3	3	0.20	1.3
60:12	0.28	–	4	3	3	3	3	2	0.20	1.4

The equilibrium data for the extraction system with ethyl acetate and ethanol mixture at 90:10 volume ratio of ethyl acetate:ethanol was then used for determining NTS that was required. The mass fraction of 1,3-PDO in the raffinate phase after extraction as a function of the number of equilibrium stages for S/F of 3.05, 5, and 9 was calculated for this case and the results (the dashed lines) are compared with that obtained without ethanol cosolvent (the solid lines) as shown in Fig. 4. Table 4 summarizes the NTS (90%) determined at various ratios for extraction with and without ethanol cosolvent, which shows that, at the S/F = 9, NTS (90%) could be reduced from 3 to 2, when the ethanol cosolvent at 90:10 volume ratio was used, compared with the extraction with ethyl acetate alone. In addition, the use of cosolvent in this case could reduce the amount of extraction solvent required considerably.

Extraction of 1,3-PDO from Actual Fermentation Broth

In this study, the extraction of the actual 1,3-PDO fermentation broth was carried out using both ethyl acetate and ethahol cosolvent at the temperature of 303.15 K. The fermentation broth was the culture of *C. butyricum* DSM 5431 in an initial concentration of glycerol of 100 g/L under anaerobic condition at 33°C and pH of 7. The concentrations of the broth used for the extraction experiment were 38.6 g/L of 1,3-PDO and 7.4 g/L of glycerol, respectively.

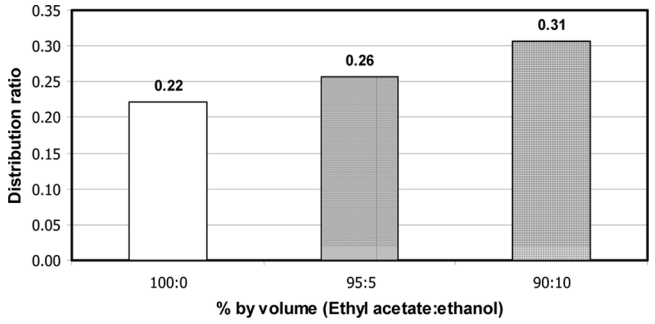

FIG. 5. Experimental distribution coefficient of 1,3-PDO extraction with ethanol cosolvent at 303.15 K.

For extraction with ethyl acetate, 20 mL of the fermentation broth was extracted with 20 mL of the solvent. The distribution coefficient of 1,3-PDO was found to be 0.14 and the selectivity of extraction of 1,3-PDO was 1.18 (Table 5). For extraction with the mixture of ethyl acetate and ethanol at the volume ratio of 90:10, the distribution coefficient of 1,3-PDO was found to increase to 0.20, while the selectivity was 1.17. From these results, For S/F ratio = 9, the NTS (90%) were determined to be 5 and 3 stages, respectively. For extraction of the actual fermentation broth, the distribution of 1,3-PDO was lower than that of the model mixture possibly due to the influence of other by-products in the fermentation broth such as acetic acid and butyric acid. Moreover, it should be noted that the final concentration of 1,3-PDO and glycerol in the fermentation broth, in this work, was close to the model mixture that was prepared at the glycerol concentration of 12 g/L, and the selectivity was also found to be similar. From these results, it is recommended that the feed from the fermentation broth should have concentration of glycerol lower 4 g/L. In addition, the extraction of 1,3-PDO should be carried out with the cosolvent at the volume ratio of ethyl acetate:ethanol of 90:10.

TABLE 4
Calculated NTS (90%) at various S/F ratios, and the total volume of solvents required for extraction of 20 ml of 40 g/L of 1,3-PDO solution

S/F	NTS (90%) with ethanol co-solvent	Amount of solvent required (ml)	NTS (90%) without ethanol co-solvent	Amount of solvent required (ml)
3.05	14	854	–	–
5	4	400	7	700
6	3	360	5	600
7	3	420	4	560
8	3	480	3	480
9	2	360	3	540
10	2	400	3	600

TABLE 5
Experimental distribution coefficients of 1,3-PDO and calculated NTS (90%) for extraction of actual fermentation broth, compared with that for model mixture (S/F = 9)

Feed	Solvent	1,3-PDO (g):glycerol (g) in 1 L feed	NTS (90%)			Selectivity ($K_{1,3\text{-PDO}}/K_{gly}$)
			$K_{D,1,3\text{-PDO}}$	S/F = 9	K_D,gly	
Model mixture	Ethyl acetate	60:4	0.23	3	0.08	2.86
Model mixture	Ethyl acetate	60:12	0.28	3	0.20	1.39
Fermentation broth	Ethyl acetate	38.6:7.4	0.14	5	0.12	1.18
Fermentation broth	Ethyl acetate: ethanol at 90:10 (v/v)	38.6:7.4	0.2	3	0.17	1.17

CONCLUSIONS

In this study, ethyl acetate was shown to be a suitable solvent for the extraction of 1,3-PDO from fermentation broth, whose distribution coefficient of 1,3-PDO at 303.15 K was found to be 0.22. The experimental distribution coefficient of 1,3-PDO did not vary significantly with temperature. The addition of glycerol in feed aqueous stream effects on the other hand increased the distribution coefficient of 1,3-PDO; however, the selectivity decreased when the concentration of glycerol increased. For extraction with the ethanol cosolvent, the distribution coefficient of 1,3-PDO increased a volume fraction of ethanol increased and the results on the extraction of actual fermentation broth at 303.15 K with ethyl acetate: ethanol at 90:10 volume ratio also showed improvement of the distribution coefficient from 0.14 and 0.20.

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