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Extraction Equilibrium of Ethanol for Bioethanol Production
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Ethanol distributions between selected organic and aqueous phases were measured for recovery and concentration of bioethanol from fermented solution. The strategy of solvent selection was based on the background of biofuel production, and *m*-xylene was selected as the primary solvent and capric acid, 1-hexanol and 2-ethyl hexanol secondary solvents were utilized to enhance the ethanol solubility. The extraction performance was evaluated through the liquid-liquid equilibrium. *m*-Xylene showed low distribution coefficient of ethanol and high separation selectivity of ethanol relative to water. All secondary solvents increased the distribution coefficient. The separation selectivity was greatly reduced by capric acid, but was similar for 1-hexanol and 2-ethyl hexanol. The two phase region was smaller for 1-hexanol than for 2-ethyl hexanol, chosen as the best secondary solvent. Examination of the effects of 2-ethyl hexanol concentration in the solvent found that a small amount of 2-ethyl hexanol could enhance the distribution coefficient and maintain the separation selectivity constant. The measured liquid-liquid equilibria were estimated with the ordinary and modified UNIFAC methods. Both methods could predict the liquid-liquid equilibrium behaviors of the measured systems, but the modified UNIFAC method could show a better correlation. However, the water concentrations in the organic phases were estimated to be larger than the measured values if the measured concentrations were very low.

Keywords

Bioethanol, Liquid-liquid equilibrium, Distribution coefficient, Mixed solvent, Separation selectivity, UNIFAC estimation

1. Introduction

Bioethanol has been recently becoming important worldwide as a gasoline substitute for transport vehicles. Processing of fermented solutions to bioethanol for use as a fuel is an energy intensive process and the conventional processes tend to be uneconomic because commodity ethanol is cheap in spite of the great difficulty in the separation of ethanol and water. The technology of bioethanol production has long been studied, and the typical method of purification is distillation^{1),2)}, which requires much energy for ethanol recovery and dehydration. 50% to 80% of the total energy is consumed in the ethanol recovery step of a typical manufacturing process, and most of this energy is consumed in distilling the ethanol to concentrations of more than 85%. Many ethanol recovery methods have been proposed to replace the distillation method, such as membrane separation³⁾, adsorption⁴⁾ and supercritical fluid extraction⁵⁾. The newly developed and conventional methods were

recently reviewed comprehensively⁶⁾.

The ordinary extraction technique has the potential to produce anhydrous ethanol from the fermented solution. Liquid-liquid equilibrium data for ethanol, water and several organic liquids have been measured at different temperatures^{7),8)}. Equilibrium distribution coefficients, defined as the concentration ratio of ethanol in the solvent phase relative to the aqueous phase, have been measured for ethanol, butanol, and acetone in various solvents, and the separation factors, defined as the distribution coefficient ratio of ethanol relative to water, have been calculated to evaluate the economic characteristics of extraction⁹⁾.

Gasoline was utilized as solvent to produce gasohol with the extractive distillation column¹⁰⁾. Heavier components in gasoline should dissolve most of the ethanol, and water and lighter components should be vaporized in the extractive column. The lighter components were recovered by decantation for separation from water and mixed with the heavier components to provide the gasohol product. This process was very effective to dehydrate the concentrated ethanol solution and the heat duties of the two reboilers were relatively

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high because the throughput of gasoline was so large relative to that of ethanol.

Selection of an appropriate solvent must involve factors depending on the Lewis acidity and steric effects¹¹⁾. Recent research on ethanol concentration with extraction technology has presented the development of an ethanol production process with novel solvents for the extractive fermentation process¹²⁾.

The present study evaluated the solvent extraction method using the methodology of preferable solvent selection and liquid-liquid equilibrium measurements. Firstly the methodology of solvent selection was used to identify preferable solvents and the liquid-liquid equilibria of ethanol in the system of ethanol, water and the selected solvent were experimentally measured at 298.15 K. The experimental results were compared with the liquid-liquid equilibria estimated by the ordinary^{13),14)} and modified¹⁵⁾ UNIFAC models. The extraction behaviors were also analyzed with respect to the ethanol distribution and separation selectivity.

2. Solvent Selection

Many organic solvents have been examined to measure the liquid-liquid equilibrium of ethanol. The properties of water and ethanol are quite similar, making solvent selection more complicated. The main factors to choose favorable solvents for ethanol extraction are as follows: boiling point of solvent, distribution coefficient of ethanol, separation selectivity of ethanol over water, and availability. Many other important criteria must be considered in selection of solvents, such as low toxicity, chemical stability, rapid phase separation (rapid settling and nonformation of stable emulsion) and so on. The first 4 factors are considered the basic criteria and the strategy of solvent selection is as follows. The boiling point of the solvent should be higher than that of ethanol to allow easy solvent recovery and the solvent should not form an azeotrope with ethanol or water. Higher distribution coefficient will result in greater extraction rate and smaller amount of required solvent in the process. The distribution coefficient of ethanol, m_{EtOH} , is defined by the Eq. (1),

$$m_{\text{EtOH}} = \frac{x_{\text{EtOH}}}{y_{\text{EtOH}}} \quad (1)$$

where x_{EtOH} and y_{EtOH} stand for the ethanol concentrations in the organic and aqueous phases at liquid-liquid equilibrium. The separation selectivity of ethanol should be higher, allowing the apparatus to be smaller and the separation operation easier. The definition of the ethanol selectivity relative to water content, $\beta_{\text{EtOH,W}}$, is given by the Eq (2),

$$\beta_{\text{EtOH,W}} = \frac{x_{\text{EtOH}}/y_{\text{EtOH}}}{x_{\text{W}}/y_{\text{W}}} \quad (2)$$

where x_{W} and y_{W} stand for the water concentrations in the organic and aqueous phases at liquid-liquid equilibrium. The selected solvent should not be special or uncommon. Bioethanol is very cheap and common, and production must allow large volume manufacturing. Therefore, the solvent should be cheap and highly available. These considerations suggest that the favorable solvent would be a hydrocarbon, with very small solubility of water. The paraffin hydrocarbons with carbon numbers greater than or equal to 9 do not form azeotropes with ethanol and have higher boiling points relative to ethanol. However, these hydrocarbons are uncommon in the general market and less available. Among the aromatics of relatively low carbon numbers, benzene and toluene form azeotropes with water. Xylene is not so expensive and does not form azeotropes with water or ethanol. Among the xylene isomers, *m*-xylene was considered to be most favorable because of the poor commercial potential in industry, so *m*-xylene was selected as the main solvent. Research on the ethanol distribution over the aqueous phase and organic phases of benzene and toluene has reported the distribution coefficients and selectivities as 0.058 and 115, and 0.040 and 100, respectively¹¹⁾. For another work these equilibrium parameters in the xylene-ethanol-water system was measured as 0.03 and 91, respectively⁸⁾. Aromatic solvents show low distribution coefficient and high separation selectivity. To improve the relatively low distribution coefficient, a second solvent to mix with *m*-xylene was employed to enhance the ethanol solubility. In this study, capric acid, 1-hexanol and 2-ethyl hexanol were selected as the second solvent from the carboxylic acids and higher alcohols. The ethanol distributions with 1-hexanol and 2-ethyl hexanol have been already reported under specified conditions^{16),17)}, and these solvents can be expected to enhance the ethanol solubility into the xylene phase.

3. Experimental Section

3.1. Materials

Special grade chemicals, ethanol, *m*-xylene, 1-hexanol, 2-ethyl hexanol and capric acid were purchased from Wako Pure Chemical Industries, Ltd. However, the purity of each compound was checked by gas chromatography before every run to confirm the mass fraction purity of higher than 0.99.

3.2. Procedure

Table 1 shows the experimental conditions for liquid-liquid equilibrium measurement. The specified amounts of the aqueous and organic phases were put in conical flasks with screw tops, and continuously shaken in the isothermal bath for 48 h, when the equilibrium condition was assumed to have been reached. The two phases were then separated with a separating funnel and the obtained solutions were analyzed by gas chroma-

Table 1 Experimental Conditions for Liquid-liquid Equilibrium Measurement

System		
organic phase	<i>m</i> -xylene, capric acid, 1-hexanol, 2-ethyl hexanol	
aqueous phase	aqueous phase of ethanol	
Conditions		
temperature	[K]	298.15
contacting time	[h]	48
volume ratio of organic and aqueous phases	[—]	1

Table 2 Liquid-liquid Equilibrium Data of Ternary Systems at 298.15 K (mass fraction)

aqueous phase			organic phase		
W	EtOH	X	W	EtOH	X
0.991	0	0.00922	0.000858	0	1
0.880	0.110	0.0106	0.000785	0.00420	0.995
0.730	0.258	0.0116	0.00120	0.0116	0.988
0.629	0.361	0.0105	0.00611	0.0254	0.968
0.461	0.511	0.0284	0.00525	0.0422	0.953
0.397	0.556	0.0475	0.00772	0.0521	0.940
0.270	0.624	0.106	0.0117	0.0818	0.907
0.094	0.502	0.404	0.0314	0.227	0.741

aqueous phase			organic phase		
W	EtOH	HxOH	W	EtOH	HxOH
0.993	0	0.00685	0.0367	0	0.963
0.945	0.0473	0.00774	0.0789	0.0393	0.882
0.870	0.121	0.00878	0.0990	0.110	0.791
0.824	0.166	0.0102	0.120	0.167	0.713
0.782	0.207	0.0113	0.151	0.216	0.633
0.751	0.232	0.0167	0.179	0.252	0.567
0.677	0.285	0.0386	0.280	0.322	0.398
0.659	0.291	0.0500	0.357	0.327	0.316

aqueous phase			organic phase			aqueous phase			organic phase		
W	EtOH	EHxOH	W	EtOH	EHxOH	W	EtOH	CA	W	EtOH	CA
0.987	0	0.0133	0.0233	0	0.977	0.989	0	0.0112	0.0547	0	0.945
0.916	0.0592	0.0246	0.028	0.0313	0.941	0.979	0.00634	0.015	0.0552	0.00448	0.94
0.854	0.118	0.0274	0.034	0.0719	0.894	0.910	0.0714	0.0186	0.112	0.0947	0.794
0.737	0.225	0.0378	0.056	0.168	0.776	0.860	0.120	0.0199	0.126	0.144	0.73
0.619	0.344	0.0371	0.122	0.326	0.551	0.801	0.176	0.0231	0.167	0.195	0.637
0.491	0.420	0.0897	0.264	0.425	0.311	0.761	0.217	0.0215	0.211	0.253	0.536
						0.734	0.239	0.0272	0.237	0.273	0.489
						0.711	0.252	0.0364	0.272	0.296	0.432

tography (Hitachi GC-663-50) with a flame ionization detector, in which the column temperature was maintained at 353 K for the initial 10 min, and then increased at 5 K/min up to 423 K. A Karl Fischer aquameter (Kyoto Electronics MKC-501) was used with dehydrated methanol of HYDRANAL methanol and titration solution of HYDRANAL composite 5, purchased from Sigma-Aldrich Co., to measure the water concentration of each solution. The measured mass fractions were determined by mass and within 0.01 errors in the mass balance of each component.

4. Results and Discussion

Tables 2 and 3 show the experimental liquid-liquid equilibrium data for the ternary and quaternary systems, respectively. Figures 1 and 2 show the ethanol distribution in the organic and aqueous phases, and the effects of the addition of the secondary solvent on the ethanol distribution. Figure 3 shows the effects of the distribution coefficient, m_{EtOH} , on the separation selectivity, $\beta_{\text{EtOH,W}}$. The *m*-xylene organic phase had the largest range of the two phase region among the selected four solvents in ternary systems. The distribution coefficients and the separation selectivities were the smallest and largest, respectively, using *m*-xylene.

Table 3 Liquid-liquid Equilibrium Data of Quaternary Systems at 298.15 K (mass fraction)

aqueous phase				organic phase			
W	EtOH	X	HeOH	W	EtOH	X	HeOH
0.995	0	0	0.0046	0.027	0	0.505	0.468
0.837	0.157	0	0.00545	0.0375	0.0851	0.426	0.45
0.763	0.230	0	0.00718	0.0558	0.154	0.403	0.387
0.654	0.320	0.000837	0.0172	0.100	0.264	0.328	0.308
0.553	0.382	0.0225	0.0418	0.158	0.339	0.261	0.239
0.403	0.426	0.0778	0.0933	0.227	0.389	0.213	0.171

aqueous phase				organic phase			
W	EtOH	X	EHxOH	W	EtOH	X	EHxOH
0.983	0	0.0114	0.0055	0.0104	0	0.508	0.481
0.878	0.0965	0.0087	0.00764	0.014	0.0335	0.500	0.453
0.810	0.173	0.0101	0.00627	0.0220	0.0739	0.466	0.438
0.735	0.249	0.00883	0.00761	0.0272	0.128	0.400	0.445
0.631	0.356	0.00603	0.00664	0.0547	0.239	0.373	0.334
0.540	0.427	0.0131	0.0203	0.0910	0.324	0.311	0.274

aqueous phase				organic phase			
W	EtOH	X	CA	W	EtOH	X	CA
0.969	0	0.0180	0.0126	0.0176	0	0.492	0.491
0.869	0.113	0.00873	0.00939	0.0236	0.0535	0.450	0.473
0.788	0.191	0.0109	0.00963	0.0428	0.118	0.411	0.428
0.742	0.236	0.00950	0.0125	0.0601	0.171	0.381	0.388
0.702	0.271	0.00967	0.0175	0.0720	0.206	0.362	0.359
0.656	0.315	0.00771	0.0215	0.0853	0.247	0.352	0.317

aqueous phase				organic phase			
W	EtOH	X	EHxOH	W	EtOH	X	EHxOH
0.985	0	0.00848	0.00621	0.0133	0	0.335	0.652
0.879	0.0994	0.0108	0.0107	0.0212	0.0442	0.324	0.610
0.816	0.160	0.0121	0.0119	0.0231	0.0800	0.303	0.594
0.769	0.214	0.00967	0.00737	0.0313	0.121	0.285	0.562
0.713	0.270	0.00767	0.00944	0.0429	0.177	0.263	0.517
0.655	0.328	0.00714	0.00926	0.0620	0.248	0.233	0.457
0.558	0.406	0.0113	0.0244	0.116	0.352	0.180	0.353
0.429	0.458	0.0346	0.0784	0.218	0.432	0.119	0.230

aqueous phase				organic phase			
W	EtOH	X	EHxOH	W	EtOH	X	EHxOH
0.986	0	0.0106	0.00312	0.00663	0	0.667	0.326
0.904	0.0830	0.0111	0.00225	0.0103	0.0232	0.667	0.300
0.807	0.178	0.0108	0.00351	0.0108	0.0548	0.645	0.289
0.733	0.250	0.0116	0.00521	0.0196	0.0940	0.615	0.272
0.661	0.320	0.0163	0.00311	0.0289	0.147	0.570	0.253
0.528	0.440	0.0153	0.01652	0.0547	0.252	0.484	0.210
0.327	0.507	0.0930	0.0720	0.123	0.384	0.333	0.160

aqueous phase				organic phase			
W	EtOH	X	EHxOH	W	EtOH	X	EHxOH
0.977	0	0.0181	0.00465	0.000499	0	0.745	0.25
0.899	0.0794	0.0168	0.005	0.00584	0.0159	0.732	0.245
0.806	0.173	0.0153	0.00588	0.00944	0.0436	0.708	0.239
0.728	0.251	0.016	0.00483	0.0125	0.077	0.682	0.228
0.655	0.323	0.0153	0.00597	0.0193	0.121	0.646	0.214
0.533	0.437	0.0158	0.0148	0.0352	0.203	0.576	0.186
0.407	0.504	0.0508	0.0378	0.0574	0.266	0.518	0.159
0.213	0.508	0.2049	0.0729	0.0729	0.317	0.505	0.105

(continued on next page)

Table 3 Liquid-liquid Equilibrium Data of Quaternary Systems at 298.15 K (mass fraction)
(continued from previous page)

aqueous phase				organic phase			
W	EtOH	X	EHxOH	W	EtOH	X	EHxOH
0.985	0	0.0136	0.00175	0.00342	0	0.843	0.153
0.909	0.0743	0.0144	0.00232	0.00443	0.0136	0.861	0.151
0.789	0.195	0.014	0.0021	0.00615	0.0348	0.812	0.147
0.709	0.272	0.0121	0.00639	0.00805	0.0596	0.789	0.143
0.635	0.349	0.0128	0.00405	0.0132	0.0945	0.856	0.136
0.603	0.381	0.0107	0.00534	0.0152	0.111	0.74	0.134
0.41	0.515	0.0471	0.028	0.0294	0.188	0.673	0.112
0.181	0.512	0.243	0.0641	0.0489	0.265	0.61	0.0763

aqueous phase				organic phase			
W	EtOH	X	EHxOH	W	EtOH	X	EHxOH
0.972	0	0.0265	0.00127	0.00128	0	0.91	0.0886
0.853	0.124	0.0206	0.00178	0.00199	0.0166	0.894	0.0873
0.764	0.209	0.0243	0.00233	0.00293	0.0264	0.884	0.0863
0.698	0.281	0.0197	0.00214	0.00414	0.0438	0.868	0.0842
0.624	0.360	0.0131	0.00313	0.00618	0.0664	0.846	0.0819
0.530	0.444	0.0174	0.00811	0.00938	0.0938	0.822	0.0747
0.381	0.543	0.0534	0.0233	0.0148	0.129	0.793	0.0635
0.128	0.468	0.360	0.0400	0.0390	0.257	0.665	0.039

aqueous phase				organic phase			
W	EtOH	X	EHxOH	W	EtOH	X	EHxOH
0.978	0	0.0168	0	0.000746	0	0.942	0.0576
0.859	0.129	0.0121	0	0.00127	0.0109	0.931	0.0566
0.798	0.188	0.0145	0	0.00163	0.0221	0.919	0.0573
0.609	0.368	0.0197	0.00323	0.00404	0.0553	0.886	0.0543
0.495	0.47	0.0262	0.0084	0.00698	0.0795	0.864	0.0494
0.396	0.539	0.0482	0.0163	0.00904	0.098	0.851	0.0418
0.104	0.473	0.397	0.0233	0.0373	0.244	0.695	0.0261

(a) *m*-xylene (X), (b) capric acid (CA), (c) 1-hexanol (HxOH) and (d) 2-ethyl hexanol (EHxOH).

Fig. 1 LLE for Ternary System of Water-ethanol-Single Solvent

(a) CA, (b) HxOH and (c) EHxOH, $y_{X,0} = 0.5$.

Fig. 2 LLE for Quaternary System of Water-ethanol-*m*-xylene and Secondary Solvent

The concentration ratio of ethanol relative to water in the organic phase was also the highest, as expected. Both ethanol and water have low solubility in *m*-xylene

solvent, but ethanol could be partitioned more easily into the *m*-xylene phase than the water phase resulting in higher selectivity. The ethanol distribution co-

Black keys: ternary systems, white keys: quaternary systems.

Fig. 3 Effects of Ethanol Distribution Coefficient on Separation Selectivity

efficients in *m*-xylene or 2-ethyl hexanol solvent were previously reported in the ranges of 2-2.5 for *m*-xylene solvent⁷⁾ and 0.66 for 2-ethyl hexanol solvent¹¹⁾. The present study found the values in the same ranges.

Capric acid dissolves water and ethanol most among the selected solvents. The two phase region was the smallest and the concentration ratio of ethanol relative to water in the organic phase was also the lowest. Although ethanol was soluble in the capric acid phase, water could also dissolve into the organic phase in high degree and the selectivity was very low.

1-Hexanol or 2-ethyl hexanol solvent had distribution coefficients larger than unity when the ethanol concentrations were in the higher range, and the selectivity decreased with higher distribution coefficient for both cases. Ethanol distributions with 1-hexanol solvent were quite similar to those for capric acid solvent. 1-Hexanol dissolved water too effectively so ethanol concentration might become difficult because of the small two phase region. The 2-ethyl hexanol-ethanol-water system had the second largest two phase region among the selected solvents and the distribution coefficient of ethanol was larger than that for *m*-xylene solvent.

As expected, *m*-xylene solvent showed higher selectivity and lower distribution coefficient for ethanol, and the two phase region was larger. The secondary solvents were employed to improve the ethanol distribution. The initial mass ratios of *m*-xylene and second solvent were fixed at 0.5 and the effects were shown in **Fig. 3** by white keys. **Figure 4** shows the effects of the distribution coefficients on the concentration ratios of ethanol relative to water content in the organic phase. The solubility of ethanol in the organic phase was significantly improved and the selectivity remained high

Fig. 4 Effects of Distribution Coefficients on Concentration Ratio of Ethanol and Water in Organic Phase ($= x_{\text{EtOH}}/x_{\text{W}}$)

for all cases. The two phase regions were smaller than in the *m*-xylene-ethanol-water system, and was smallest for capric acid as the second solvent, followed by 1-hexanol and 2-ethyl hexanol. Addition of the second solvent increased the distribution coefficient and slightly reduced the selectivity. The effects of the second solvent type on both distribution coefficient and selectivity were indistinct, but the two phase region was the largest for 2-ethyl hexanol. 2-Ethyl hexanol is the most commercially available of the three second solvents. Therefore, *m*-xylene and 2-ethyl hexanol were selected as the primary and secondary solvents, respectively. The ethanol distribution over the water and selected mixed solvent phases was then investigated further.

Figures 5 and 6 show the effects of *m*-xylene to 2-ethyl hexanol ratio on the ethanol distribution. Greater 2-ethyl hexanol content increased the distribution coefficient but reduced the two phase region and the ethanol selectivity. The addition of only a small amount of 2-ethyl hexanol improved the ethanol distribution performance. The distribution coefficients were higher and the separation selectivities were remained almost constant. The favorable solvent concentration should be selected depending on the process specifications to separate and concentrate ethanol from aqueous solution.

Finally the ethanol distribution behaviors were estimated by thermodynamic modeling. The UNIFAC method is one of the most common methods applied to much research on the ethanol distribution over the aqueous and organic phases. In this study, the ordinary¹⁴⁾ and modified¹⁵⁾ UNFAC methods were used to predict the distribution behaviors. The UNIFAC method cannot easily estimate the activity coefficients of high polar components, such as water, in many cases. Therefore, all mass fractions except for water were estimated

based on the activity coefficients from the UNIFAC methods, and the mass fractions of water were estimated from the material balance equations in this study. **Figures 1, 2 and 5** show the predictions by the ordinary and modified UNIFAC models. The root-mean-square deviations (RMSD) are listed in **Table 4**, estimated with the Eq. (3)^{18),19)};

$$\text{RMSD} = \left[\frac{\sum_i (x_i^{\text{exp}} - x_i^{\text{calc}})^2 + \sum_i (y_i^{\text{exp}} - y_i^{\text{calc}})^2}{6M} \right]^{1/2} \quad (3)$$

where M is the total number of tie lines. Actually the NRTL model was also employed to evaluate the prediction. However, the deviations from the NRTL model were very large and only the results of the UNIFAC methods were discussed here. Both UNIFAC methods were very flexible to estimate the ethanol distribution

behaviors, but the modified UNIFAC method was better. Overall, if water concentrations were low in the organic phases of *m*-xylene or higher *m*-xylene content, the estimated water contents in the organic phase were 10% to 30% larger than the experimental values, because the actual concentrations of water in the organic phase were very small and difficult to predict. However, prediction of the ethanol behavior might be enough satisfactory, and the modified UNIFAC method was verified to be better one.

5. Conclusions

The solvent selection strategy suggested that hydrocarbons would show higher separation selectivity and *m*-xylene was selected as the primary solvent based on separation performance and availability. The separation selectivity is very high but the distribution coefficient is low. Therefore, a secondary solvent was employed to enhance the ethanol solubility, and capric acid, 1-hexanol and 2-ethyl hexanol were chosen from the carboxylic acids and higher alcohols. Addition of these secondary solvents enhanced the distribution coefficient but capric acid reduced the separation selectivity.

(a) $y_{X,0} = 0.35$, (b) $y_{X,0} = 0.67$, (c) $y_{X,0} = 0.76$, (d) $y_{X,0} = 0.84$, (e) $y_{X,0} = 0.91$ and (f) $y_{X,0} = 0.94$.

Fig. 5 LLE for Quaternary System of Water-ethanol-*m*-xylene and 2-Ethyl Hexanol

Primary solvent: *m*-xylene, secondary solvent: 2-ethyl hexanol.

Fig. 6 Effects of 2-Ethyl Hexanol Addition to Organic Phase on Separation Selectivity

Table 4 List of RMSD Values

System	Ordinary UNIFAC	Modified UNIFAC
<i>m</i> -xylene-ethanol-water	0.0305	0.0221
capric acid-ethanol-water	0.0331	0.0265
1-hexanol-ethanol-water	0.0286	0.0225
2-ethyl hexanol-ethanol-water	0.0301	0.0201
<i>m</i> -xylene-capric acid-ethanol-water	0.0341	0.0231
<i>m</i> -xylene-1-hexanol-ethanol-water	0.0312	0.0275
<i>m</i> -xylene-2-ethyl hexanol-ethanol-water	0.0322	0.0234

The distribution coefficients and separation selectivities using 1-hexanol and 2-ethyl hexanol were quite similar but the two phase region was smaller with 1-hexanol than with 2-ethyl hexanol. The effects of 2-ethyl hexanol concentration on the ethanol distribution over the organic and aqueous phases were examined. The addition of a small amount of 2-ethyl hexanol to *m*-xylene enhanced the distribution coefficient with constant separation selectivity.

The liquid-liquid equilibria measured in this study were estimated with the ordinary and modified UNIFAC methods and the modified UNIFAC method provided estimates. However, the regions of very small water concentrations in the organic phase were difficult to estimate even with the modified UNIFAC method. These regions are very important for the ethanol dehydration process and further development of the estimation technique is essential.

Nomenclatures

m_i	: distribution coefficient of component i , defined as Eq. (1)	[—]
RMSD	: root-mean-square deviation, defined as Eq. (3)	[—]
x_i	: mass fraction of component i in organic phase	[—]
y_i	: mass fraction of component i in aqueous phase	[—]
$\beta_{i,j}$	: separation selectivity, defined as Eq. (2)	[—]
<Symbols>		
CA	: capric acid	
EtOH	: ethanol	
EHxOH	: 2-ethyl hexanol	
HxOH	: 1-hexanol	
X	: <i>m</i> -xylene	
<Superscripts>		
cal	: calculated value	
exp	: experimental value	
<Subscripts>		
i, j	: component i or j	
0	: initial	

References

- 1) Black, C., *Chem. Eng. Prog.*, **76**, 78 (1980).
- 2) Luyben, W. L., *AIChE J.*, **52**, (2), 623 (2006).
- 3) Morigami, Y., Kondo, M., Abe, J., Kita, H., Okamoto, K., *Sep. Purif. Technol.*, **25**, (1–3), 251 (2001).
- 4) Al-Asheh, S., Ganat, F., Al-Lagtah, N., *Chem. Eng. Res. Des.*, **82**, (A7), 855 (2004).
- 5) Diaz, S., Gros, H., Brignole, E. A., *Computers and Chemical Engineering*, **24**, (9–10), 2069 (2000).
- 6) Huang, H., Ramaswamy, S., Tschirner, U. W., Ramarao, B. V., *Sep. Purif. Technol.*, **62**, 1 (2008).
- 7) Roddy, J. W., *Ind. Eng. Chem., Process Des. Dev.*, **20**, (3), 104 (1981).
- 8) Roddy, J. W., Coleman C. F., *Ind. Eng. Chem., Fund.*, **20**, (3), 250 (1981).
- 9) Dadgar, A. M., Foutch, G. L., *Biotech. Bioeng. Symp.*, **15**, (15), 611 (1985).
- 10) Chianese, A., Zinamosca, F., *Chem. Eng. J.*, **43**, 59 (1990).
- 11) Munson, C. L., Judson, C. K., *Ind. Eng. Chem., Process Des. Dev.*, **23**, 109 (1984).
- 12) Richard, D. O., Stephenson, S. K., Franqui, D., Cline, J. L., Robertson, G. H., Orts, W. J., *Sep. Purif. Technol.*, **63**, 444 (2008).
- 13) Magnussen, T., Rasmussen, P., Fredenslund, A., *Ind. Eng. Chem., Process Des. Dev.*, **20**, 331 (1981).
- 14) Gmehling, J., Rasmussen, P., Fredenslund, A., *Ind. Eng. Chem., Process Des. Dev.*, **21**, 118 (1982).
- 15) Larsen, B. L., Rasmussen, P., Fredenslund, A., *Ind. Eng. Chem., Res.*, **26**, (11), 2274 (1987).
- 16) Egan, B. Z., Lee, D. D., McWhirter, D. A., *Ind. Eng. Chem., Res.*, **27**, (7), 1330 (1988).
- 17) Koullas, D. P., Umealu, O. S., Koukios, E. G., *Sep. Sci. and Tech.*, **34**, (11), 2153 (1999).
- 18) Alijimiz, A. S., Fandary, M. S. H., Alkandary, J. A., *J. Chem. Eng. Data*, **45**, 301 (2000).
- 19) Mohsen-Nia, M., Modarress, H., Doulabi, F., *Fluid Phase Equilib.*, **239**, 1 (2006).

要 旨

バイオエタノール製造のためのエタノールの抽出平衡
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発酵溶液からのバイオエタノールの分離・濃縮を目的とし、選定した溶媒を用いてエタノールの液液分配平衡を測定した。まず、製品がバイオ燃料であることを考慮し溶媒選択の方針を示した。*m*-キシレンを主溶媒とし、補溶媒をこれに混合することによりエタノールの溶解度を向上させることとした。カプリン酸, 1-ヘキサノール, 2-エチルヘキサノールを補溶媒として4成分系液液平衡を測定し、エタノールの抽出性能を評価した。主溶媒の*m*-キシレンのみを用いた3成分系液液平衡の場合、エタノールの分配係数は小さく、水に対するエタノールの選択度は高かった。補溶媒を使用した場合全てにおいて分配係数は向上したが、カプリン酸を用いた場合は分離の選択度が非常に低下した。1-ヘキサノールおよび2-エチルヘキサノールを用い

た場合の分離の選択度には大きな違いはなかったが、1-ヘキサノールを用いた場合の方が2-エチルヘキサノールを用いた場合に比べて2相領域が小さく、2-エチルヘキサノールがより適した補溶媒であった。次に、2-エチルヘキサノールの濃度によるエタノールの分配への影響を測定した。少量の2-エチルヘキサノールの添加により分配係数は向上し、かつ分離の選択度は*m*-キシレンの場合のものと同等であった。また、一般および改定 UNIFAC 法を用いて測定した液液平衡を推定した。両方法は十分に液液平衡を満足に予測することができたが、改定 UNIFAC 法がより良い予測をした。しかし、濃度の低い範囲における油相中の水濃度の推算は難しく、実測値より大きく推算した。

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