Phase Equilibrium of Biodiesel Compounds for the Triolein + Palmitic Acid + Methanol System with Dimethyl Ether as Cosolvent

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In biodiesel production, transesterification in a homogeneous mixture is possible if a solution of triolein and methanol could be prepared with the use of a cosolvent. The volatile solvent dimethyl ether (DME) can make the immiscible mixture of triolein and methanol miscible; moreover, it can be easily recovered due to its high volatility after reaction. Therefore, the vapor–liquid–liquid equilibrium for the triolein + fatty acid−methanol + DME system was measured by determining the liquid composition, temperature, and pressure of the system. Results showed that DME and palmitic acid effectively promoted the mutual solubilities of triolein and methanol. In addition, the UNIFAC prediction was compared with experimental data, and it was found that the UNIFAC model could represent the complicated phase equilibrium of biodiesel compounds.

Introduction

It is expected that petroleum resources will become markedly depleted in the 21st century. Thus, the development of future alternative energy resources is crucial to human survival. One such initiative is the utilization of oils used in the food industry as fuel. In general, biodiesel can be generated by the transesterification of triolein and methanol using a base catalyst. Hence, the essential objective of biodiesel production is to promote such transesterification. Boocock et al.[1] have suggested that the use of tetrahydrofuran (THF) enables the formation of a solution from triolein and methanol with the use of a base catalyst and induces the rapid formation of methyl ester from vegetable oils. They have also reported the detailed compositions of monoglycerides, diglycerides, and triglycerides in the transesterification with THF.[2] On the other hand, He et al.[3] reported the no catalyst transesterification using supercritical methanol and that the use of supercritical methanol can shorten transesterification time. We examined the use of dimethyl ether (DME) as a cosolvent of both triolein and methanol and found that it could produce a homogeneous solution from the three components with the use of a base catalyst. The transesterification with DME was 100 times faster than that without DME.[4] An important feature required for such superfast transesterification is the homogeneity or complete miscibility of the solution used. Another approach to the production of biodiesel is the use of a mixture of petrodiesel, biodiesel, and methanol. Kwanchareon et al. discussed the solubility properties of methanol for use in conventional diesel engines.[5] Recently, Marchettu et al.[6] reviewed some possibilities of biodiesel production.

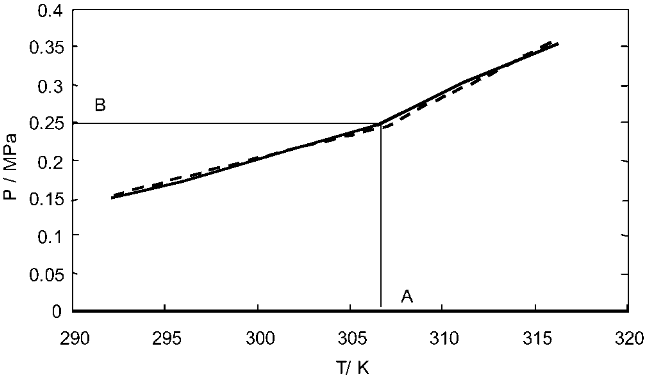

Figure 1. Typical temperature and pressure changes during cooling (dashed line) and heating (continuous line).

The solubility properties of biodiesel components such as vegetable oil, alcohol, glycerin, and other fats have become an important problem to solve. A typical biodiesel mixture contains triolein, fatty acids, methanol, and glycerin. Before transesterification, trolein and methanol form an immiscible solution. DME can make the immiscible solution homogeneous. Therefore, a quantitative amount of DME to make a homogeneous mixture is needed. DME is a volatile, hydrophilic, gaseous solvent. It can be easily recovered after transesterification and recycled. The solubility properties of a mixture of triolein and methanol with DME should be in a vapor–liquid–liquid three-phase equilibrium because triolein and methanol form an immiscible liquid and DME has high volatility in the system. We measured the pressure P, temperature T, and liquid composition x when the homogeneous solution became immiscible and compared the experimental data with the predicted values using the UNIFAC model[7,8] which we found useful for predicting the phase equilibrium of biodiesel-relevant systems in our previous work.[9]

Experimental

Materials. Triolein from Kanto Chemical Co. was used without further purification, and its purity by gas chromatog-

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Table 1. Liquid–Liquid Phase Equilibrium Data for the Ternary DME (1) + Triolein (2) + Methanol (4) System

	triolein phase			boundary point	
x_4/x_2	x_1	x_2	x_4	T_e/K	P_e/MPa
3	–	0.25	0.75	317.85	0.051
	0.362	0.16	0.478	307.65	0.256
	0.475	0.131	0.394	304.35	0.314
	0.57	0.108	0.322	286.65	0.229
4	0.196	0.159	0.645	347.35	0.392
	0.404	0.118	0.478	330.35	0.481
	0.508	0.097	0.395	311.35	0.435
5	0.209	0.132	0.659	360.75	0.560
	0.359	0.107	0.534	336.05	0.527
	0.478	0.088	0.434	315.35	0.446
6	0.167	0.12	0.713	373.35	0.588
	0.396	0.086	0.518	345.45	0.658
	0.474	0.075	0.451	318.85	0.498

Table 2. Liquid–Liquid Phase Equilibrium Data for the Quaternary DME (1) + Triolein (2) + Palmitic acid (3) + Methanol (4) System, $x_3/(x_2 + x_3) = 0.28$

	triolein phase				boundary point	
$x_4/(x_2 + x_3)$	x_1	x_2	x_3	x_4	T_e/K	P_e/MPa
2.2	–	0.23	0.08	0.69	317.85	0.051
	0.233	0.177	0.061	0.529	311.25	0.176
	0.524	0.11	0.037	0.329	283.25	0.181
4	0.172	0.119	0.045	0.664	309.85	0.155
	0.25	0.109	0.041	0.6	308.65	0.199
	0.378	0.09	0.035	0.497	291.45	0.192
	0.529	0.068	0.026	0.377	280.85	0.198
5	0.23	0.093	0.036	0.641	320.45	0.260
	0.35	0.079	0.031	0.54	305.45	0.264
	0.47	0.064	0.025	0.441	284.75	0.205
6	0.155	0.088	0.033	0.724	339.85	0.311
	0.273	0.075	0.029	0.623	326.85	0.362
	0.463	0.056	0.021	0.46	286.85	0.220

raphy was higher than w = 90 %. Methanol from Kanto Chemical Co. was used as received, with its purity guaranteed at more than w = 99 %. Palmitic acid from Kanto Chemical was used with a guaranteed purity at more than w = 98 %. DME from GL Science Co. was used, and its purity was higher than w = 99 %.

Experimental Procedure. The experimental apparatus used was described elsewhere.[10] The experiment was conducted as follows. About 0.04 kg of a mixture of triolein, palmitic acid, and methanol (each of known mole fractions) was fed into a glass cell (TAIATSU glass V100) capable of withstanding a pressure of 2.0 MPa. The cell was evacuated after the mixture was frozen at liquid nitrogen temperature. DME was then fed into the glass cell from the liquefied gas reservoir. The mass of liquefied gas in the solution was determined from the change in the mass of the liquefied gas reservoir. The mole fractions of all the components of the solution were calculated from the masses of all components of the feed.

The slurry in the pressurized glass cell was agitated at 400 rpm, and the temperature of the solution was controlled by a film-heater on the glass cell. The slurry was heated to a certain temperature to dissolve the solid phase in the solution. After

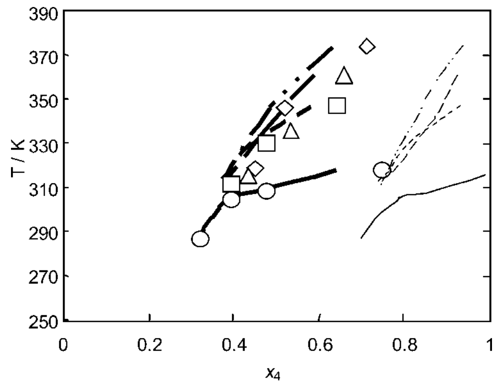

Figure 2. Liquid–liquid equilibrium for the ternary DME (1) + triolein (2) + methanol (4) system: -○-, x_4/x_2 = 3; -□-, x_4/x_2 = 4; -Δ-, x_4/x_2 = 5; -◇-, x_4/x_2 = 6. Points are experimental data, and the other curves are LLE UNIFAC predictions.

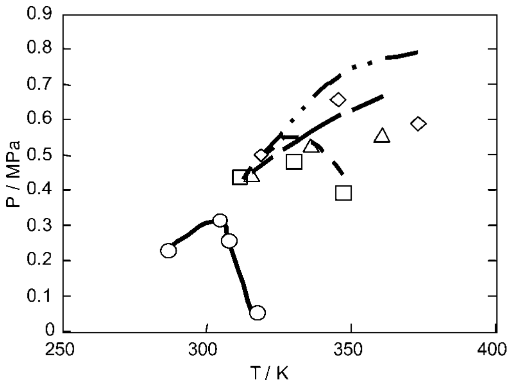

Figure 3. Liquid–liquid equilibrium for the ternary DME (1) + triolein (2) + methanol (4) system: -○-, x_4/x_2 = 3; -□-, x_4/x_2 = 4; -Δ-, x_4/x_2 = 5; -◇-, x_4/x_2 = 6. Points are experimental data, and the other curves are LLE UNIFAC predictions.

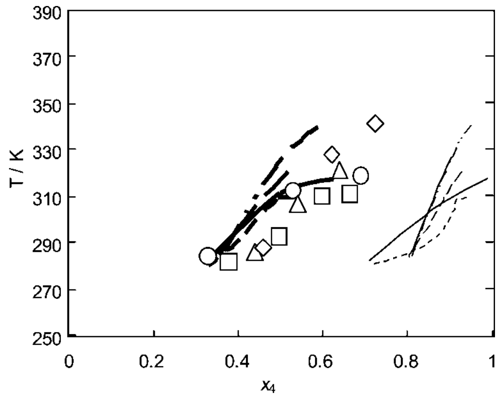

Figure 4. Liquid–liquid equilibrium for the quaternary DME (1) + triolein (2) + palmitic acid (3) + methanol (4) system: -○-, $x_4/(x_2 + x_3)$ = 2.2; -□-, $x_4/(x_2 + x_3)$ = 4; -Δ-, $x_4/(x_2 + x_3)$ = 5; -◇-, $x_4/(x_2 + x_3)$ = 6. Points are experimental data, and the other curves are LLE UNIFAC predictions.

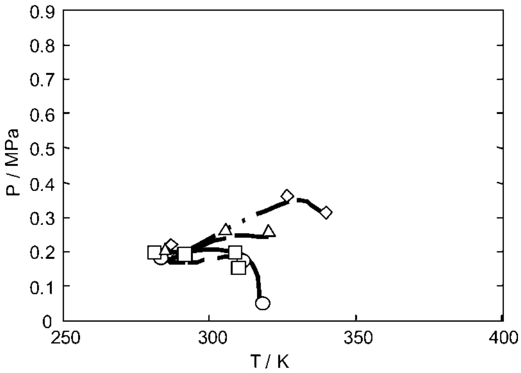

Figure 5. Liquid–liquid equilibrium for the quaternary DME (1) + triolein (2) + palmitic acid (3) + methanol (4) system: -○-, $x_4/(x_2 + x_3)$ = 2.2; -□-, $x_4/(x_2 + x_3)$ = 4; -Δ-, $x_4/(x_2 + x_3)$ = 5; -◇-, $x_4/(x_2 + x_3)$ = 6. Points are experimental data, and the other curves are LLE UNIFAC predictions.

Table 3. Mugnussen's UNIFAC Parameter Table

		CH_3O	CH_3	CH	CH_2	CH_2COO	CH=CH	COOH	OH
CH_3O	a	0	1571	1571	1571	461.3	76.44	1402	137.1
CH_3	a	662.1	0	0	0	972.4	74.54	139.4	644.6
CH	a	662.1	0	0	0	972.4	74.54	139.4	644.6
CH_2	a	662.1	0	0	0	972.4	74.54	139.4	644.6
CH_2COO	a	−235.7	−320.1	−320.1	−320.1	0	485.6	1417	180.6
CH=CH	a	289.3	292.3	292.3	292.3	−577.5	0	1647	724.4
COOH	a	−96.62	1744	1744	1744	−117.6	−48.52	0	118.4
OH	a	262.5	328.2	328.2	328.2	195.6	470.7	−104	0

the vapor–liquid–liquid three-phase equilibrium (VLLE) was established, the heterogeneous solution was slowly heated at 0.5 $K \cdot min^{-1}$ until it became homogeneous. The resulting solution was cooled at 0.5 $K \cdot min^{-1}$ until it became heterogeneous again. The variations in temperature and pressure during heating and cooling were measured using a platinum resistance thermometer and a pressure gauge (Delta Ohm, Inc., Italy), respectively. The temperature and pressure data were entered automatically into a data logger. The platinum resistance thermometer was calibrated using the melting and boiling temperatures of distilled water (based on ITS-90). The pressure gauge was calibrated using the vapor pressure of pure 2-methylpropane represented by the Wagner equation.[11] The uncertainties of temperature and pressure were within 0.1 K and 10 kPa, respectively. Typical temperature and pressure plots for the solution during cooling are shown in Figure 1. Point A on the heating and cooling curves was the same as the equilibrium temperature T_e. The equilibrium pressure P_e was considered as point B, which marks the VLLE on the heating and cooling curves between the heterogeneous and homogeneous states of the solution. The equilibrium temperatures were reproducible to within 0.5 K, whereas the equilibrium pressures were reproducible to within 10 kPa during heating and cooling processes. The uncertainty of the mole fractions in the solution was ± 0.01.

Experimental Results

The VLLE data (13 points) for the DME (1) + triolein (2) + methanol (4) system are listed in Table 1. The T_e, x_4 phase diagram for ternary VLLE is shown in Figure 2. As the mole ratio of methanol to triolein increased in the mixture, the temperature of the two-liquid-phase region also increased. When the DME content in the mixture increased or x_4 decreased, the temperature of the heterogeneous region decreased and converged for all mole ratios of methanol to triolein. The P_e, T_e

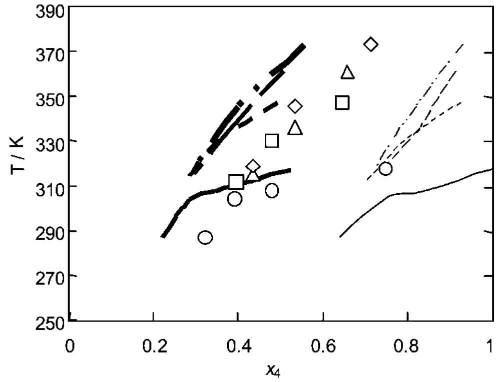

Figure 6. Liquid–liquid equilibrium for the ternary DME (1) + triolein (2) + methanol (4) system: -○-, $x_4/x_2 = 3$; -□-, $x_4/x_2 = 4$; -Δ-, $x_4/x_2 = 5$; -◇-, $x_4/x_2 = 6$. Points are experimental data, and the other curves are Gmehling's UNIFAC predictions.

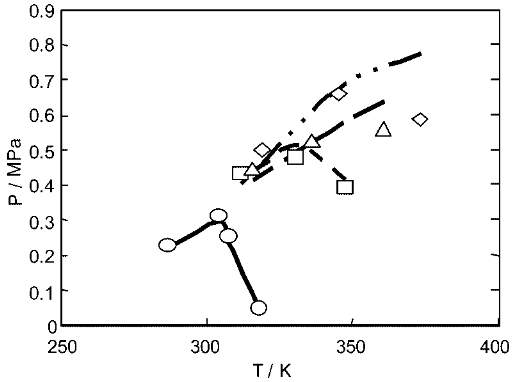

Figure 7. Liquid–liquid equilibrium for the ternary DME (1) + triolein (2) + methanol (4) system: -○-, $x_4/x_2 = 3$; -□-, $x_4/x_2 = 4$; -Δ-, $x_4/x_2 = 5$; -◇-, $x_4/x_2 = 6$. Points are experimental data, and the other curves are Gmehling's UNIFAC predictions.

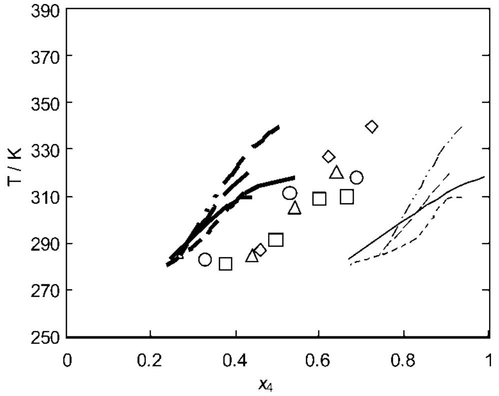

Figure 8. Liquid–liquid equilibrium for the quaternary DME (1) + triolein (2) + palmitic acid (3) + methanol (4) system: -○-, $x_4/(x_2 + x_3) = 2.2$; -□-, $x_4/(x_2 + x_3) = 4$; -Δ-, $x_4/(x_2 + x_3) = 5$; -◇-, $x_4/(x_2 + x_3) = 6$. Points are experimental data, and the other curves are Gmehling's UNIFAC predictions.

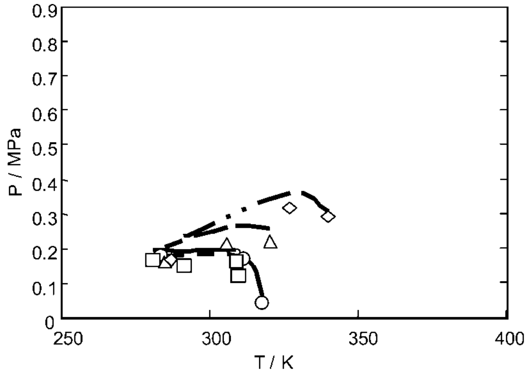

Figure 9. Liquid–liquid equilibrium for the quaternary DME (1) + triolein (2) + palmitic acid (3) + methanol (4) system: -○-, $x_4/(x_2 + x_3) = 2.2$; -□-, $x_4/(x_2 + x_3) = 4$; -Δ-, $x_4/(x_2 + x_3) = 5$; -◇-, $x_4/(x_2 + x_3) = 6$. Points are experimental data, and the other curves are Gmehling's UNIFAC predictions.

Table 4. Gmehling's UNIFAC Parameter Table

		CH_3O	CH_3	CH	CH_2	CH_2COO	CH=CH	COOH	CH_3OH
CH_3O	a	0	−9.65	−9.65	−9.65	824.2	−844.3	521.48	475.2
	b	0	−0.03	−0.03	−0.03	−6.01	2.94	0	0.12
	c	0	0	0	0	0.01	0	0	0
CH_3	a	233.1	0	0	0	98.66	189.66	1182.2	2409.4
	b	−0.32	0	0	0	1.93	−0.27	−3.26	−3.01
	c	0	0	0	0	0	0	0.01	0
CH	a	233.1	0	0	0	98.66	189.66	1182.2	2409.4
	b	−0.32	0	0	0	1.93	−0.27	−3.26	−3.01
	c	0	0	0	0	0	0	0.01	0
CH_2	a	233.1	0	0	0	98.66	189.66	1182.2	2409.4
	b	−0.32	0	0	0	1.93	−0.27	−3.26	−3.01
	c	0	0	0	0	0	0	0.01	0
CH_2COO	a	195.3	632.22	632.22	632.22	0	−582.82	62.03	294.76
	b	−9.75	−3.39	−3.39	−3.39	0	1.67	1.06	0.37
	c	0.04	0	0	0	0	0	0	0
CH=CH	a	733.3	−95.42	−95.42	−95.42	980.74	2026.10	−628.07	
	b	−2.51	0.06	0.06	0.06	−2.42	0	8.15	10
	c	0	0	0	0	0	0	0	−0.01
COOH	a	−310.82	2017.7	2017.7	2017.7	59.59	−347.5	0	1075.5
	b	0	−9.09	−9.09	−9.09	−0.71	1.22	0	−3.43
	c	0	0.01	0.01	0.01	0	0	0	0
CH_3OH	a	−87.48	82.59	82.59	82.59	299.23	−96.3	−733.07	0
	b	−0.55	−0.49	−0.49	−0.49	−1.27	0.63	2.34	0
	c	0	0	0	0	0	0	0	0

phase diagram for the ternary VLLE is shown in Figure 3. As the mole ratio of methanol to triolein increased in the mixture, the temperature of the two-liquid-phase region as well as pressure also increased. However, there is a maximum pressure beyond which no further pressure increase is possible. The pressure in the VLLE decreased as temperature increased because DME dissolved well in the homogeneous solution. The VLLE data (13 points) for the DME (1) + triolein (2) + palmitic acid (3) + methanol (4) system are listed in Table 2. All data are for the mixtures containing $w = 10$ % palmitic acid against triolein or $x_3/(x_2 + x_3) = 0.28$. The T_e, x_4 phase diagrams for the quaternary VLLE are shown in Figure 4. Note that palmitic acid could serve as a cosolvent of heterogeneous mixtures of methanol and triolein of any ratios. Compared with that shown in Figure 2, the temperature of the two-liquid-phase region decreased. As the DME content in the mixture increased or x_4 decreased, the temperature of the heterogeneous region also decreased. The P_e, T_e phase diagram for the quaternary VLLE is shown in Figure 5. As the mole ratio of methanol to triolein in the mixture increased, the temperature of the two-liquid-phase region as well as pressure slightly increased. However, the pressure of VLLE was very low compared with that shown in Figure 3. Palmitic acid strongly promoted the miscibility of triolein and methanol with DME.

UNIFAC Prediction

The prediction of the phase equilibrium of multiphases of a multicomponent system is quite difficult using a graphical plot. An activity coefficient model is essential for the analysis of such complex mixtures. The UNIFAC method has been developed for the prediction of organic compounds used in the petrochemical industry; it remains the only method used in predicting activity coefficients. Here, we examined the prediction of complex phase equilibrium in biochemical compounds by the UNIFAC method. As for VLLE, liquid–liquid and vapor–liquid equilibrium are established simultaneously. The equation of LLE for all components in the mixture is

$$\ln \gamma_i^{o} x_i^{o} = \ln \gamma_i^{a} x_i^{a} \tag{1}$$

where x_i and γ_i denote the mole fraction and activity coefficient of component i. The superscripts o and a indicate the triolein- and methanol-rich phases, respectively. The equation of VLE is given by the general Raoult equation

$$P_e = \sum_i p_i^{sat} x_i^{a} \gamma_i^{a} \tag{2}$$

where P_e and P^{sat} are the total pressure and vapor pressure of pure component i, respectively. Vapor pressure is calculated as a function of temperature T_e as described in ref 11.

The measured variables in this study are temperature T_e, pressure P_e, and mole fractions of the triolein phase x^{o}. The mole fractions of the methanol phase are not obtained in this study. For the prediction of LLE by eq 1 with the UNIFAC method, we assumed that two mole fractions of the triolein phase would be fixed at the same values as the experimental data. The predicted mole fractions of methanol and palmitic acid in the triolein phase can be compared with experimental data. The predicted vapor pressure of VLLE is calculated by eq 2 when eq 1 is satisfied in the system.

The UNIFAC is a group solution model whose original functional groups can compose a system containing DME, triolein, palmitic acid, and methanol. However, the interaction parameters of the UNIFAC in this study used Mugnussen's parameters[7] because they are very effective for LLE. The predicted curves in Figures 2 to 5 were calculated using eqs 1 and 2 with the UNIFAC model. The results of qualitative prediction were good. The effects of DME and palmitic acid on the miscibility of triolein and methanol were well represented. The difference between experimental data and the UNIFAC prediction might be caused by the bad purity of triolein, $w = 90$ %. However, its purity can be modified by the number of CH functional groups of UNIFAC. The CH functional group of UNIFAC cannot affect the activity coefficients in the solution much. It can be thought that the purity of triolein also does not change transition points much. The parameter table of Mugnussen's UNIFAC is listed in Table 3. We also examined Gmehling's parameters[8] as functions of temperature, the results of which are shown in Figures 6 to 9. The predicted pressure was good, but the mole fractions of methanol of the triolein phase were not in good agreement with experimental data. This might be the reason Gmehling's parameters can be used for both VLE and LLE systems. The parameter table of Gmehling's UNIFAC is listed in Table 4.

Conclusion

The phase equilibrium of VLLE for the DME (1) + triolein (2) + palmitic acid (3) + methanol (4) system was measured. It was found experimentally that the miscibility of triolein and methanol increased as the contents of the volatile cosolvent DME and additional palmitic acid increased in the solution. Those effects of DME and palmitic acid could be expressed by the thermodynamic equations with the UNIFAC model.

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