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Application of a ternary phase diagram to the liquid-liquid extraction of ethanoic acid using ethyl ethanoate

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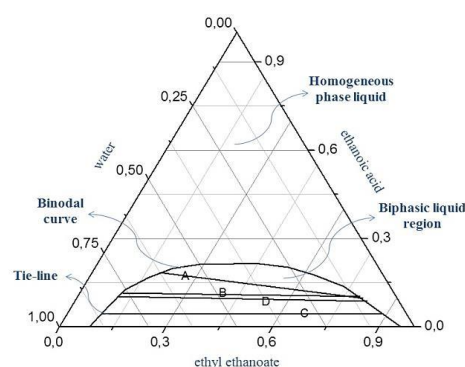
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ABSTRACT: This article describes the liquid-liquid equilibrium of the extraction process of ethanoic acid ($C_2H_4O_2$) in aqueous phase using ethyl ethanoate as the solvent. The liquid-liquid extraction was modeled by the construction of a ternary phase diagram for the water/ethanoic acid/ethyl ethanoate system using the Origin software. The equilibrium data were experimentally obtained by titration at room temperature (298.15 K) and atmospheric pressure (101325 Pa) using four mixtures of water, ethanoic acid, and ethyl ethanoate. The determination of the composition of the extract and residue portions in the equilibrium of each mixture by of the tie-lines method allowed to examine the percentages of liquid-liquid extraction achieved. The distribution coefficients and separation factors calculated, made it possible an evaluation of the distribution and of the mutual solubility of the solute in the aqueous and organic phases. The results showed a good performance of ethyl ethanoate in the extraction of ethanoic acid for concentrations of solute until 16% of the feed.



Ternary phase diagram for the water-ethanoic acid-ethyl ethanoate system

1. Introduction

Ethanoic acid ($C_2H_4O_2$) is one of the most widely used and important carboxylic acids in the world. Its wide range of applications includes its use as a raw material in the production of polymers derived from vinyl acetate, purified terephthalic acid, and esters of acetic anhydride and acetate, and as a solvent in the production of cellulose acetate and in the manufacture of pharmaceutical products^{1,2}. Its global market demand was 13 million tons in 2015 and is forecast to reach 18 million tons by 2020³.

The separation of the mixture of ethanoic acid and water is of great economic importance but is particularly difficult because it forms a pinch azeotrope. It is not a real azeotropic mixture, but the equilibrium concentrations of its constituents

are very close and therefore requires many stages. For mixtures with concentrations below 40% ethanoic acid, the liquid-liquid extraction process is the most appropriate¹.

Liquid-liquid extraction (LLE) is an important unitary operation employed in the chemical industry due to its high efficiency and low energy consumption and environmental impact. It is one of the most important mass transfer processes in chemical engineering and an alternative method to distillation⁴. Its efficiency is based on the physical and chemical properties of a solvent (organic phase) used to separate, purify or concentrate a certain constituent of an aqueous phase^{5,6}.

To design and optimize the LLE, liquid-liquid equilibrium data provided by ternary phase diagrams involving a solubility curve and tie-lines are required⁵. From the industrial point of view,

knowledge of phase equilibrium is essential in modern process design and control methods⁴. Liquid-liquid equilibrium studies of systems composed of water, phenolic compounds and organic solvents are necessary for the evaluation of industrial units for solvent extraction processes⁷.

The equilibrium behavior of a three-component liquid-liquid system is typically described using a ternary phase diagram where experimental solubility data are plotted as points, which in turn lie in the binodal curve. The ternary phase diagram consists of an equilateral triangle where each side is divided into equal parts, corresponding to the mass fractions of each component of the system. The sides of the triangle represent the binary mixtures, while the vertices correspond to the pure components. Within the binodal curve, the biphasic liquid region is located, as well as the tie-lines that join the extract and residue streams in equilibrium, and outside, the homogeneous phase region⁸⁻¹⁰.

The spectrum of potential solvents for separation processes involving liquid-liquid extraction includes ethyl ethanoate, which has excellent properties for industrial applications, as well as being environmentally friendly and low cost, low toxicity and chemical stability¹¹. Ethyl ethanoate has low toxicity compared to most organic solvents (benzene, toluene, chloroform) and its saturation temperature is considerably lower than other low toxicity solvents¹².

In this context, based with the increasing worldwide demand for ethanoic acid, as well as in advantages of the use of ethyl ethanoate, the present article aims at studying the application of ternary phase diagram to the liquid-liquid extraction of ethanoic acid from aqueous phase using ethyl ethanoate as the solvent.

2. Materials and methods

2.1 Binodal curve construction

The liquid-liquid extraction process of ethanoic acid ($C_2H_4O_2$) realized was modeled by the construction of a ternary phase diagram for the water/ethanoic acid/ethyl ethanoate system at room temperature (298.15 K) and atmospheric pressure (101325 Pa). Initially, six points of the binodal curve for the water-rich phase were created by titration with ethyl ethanoate using 25.00 mL of water and the volumes of 0.00; 2.00; 4.00; 6.00; 8.00, and 10.00 mL of ethanoic acid in each point. The volumes of ethyl ethanoate, required for the

turbidity of the aqueous solution containing ethanoic acid, were experimentally obtained and presented in Table 1. Subsequently, more seven points were created for the ethyl ethanoate-rich phase. For this, 25.00 mL of ethyl ethanoate and 0.00; 2.00; 4.00; 6.00; 8.00, 10.00 and 12.00 mL of ethanoic acid were used. The water expenses volumes were presented in Table 2.

Table 1. Experimental data of water-rich phase at T = 298.15 K under P = 101325 Pa.

Point	Volumes (mL)		
	Water	Ethanoic acid	Ethyl ethanoate
1	25.00	0.00	2.50
2		2.00	3.50
3		4.00	4.50
4		6.00	7.00
5		8.00	10.40
6		10.00	15.90

Table 2. Experimental data of ethyl ethanoate-rich phase at T = 298.15 K under P = 101325 Pa.

Point	Volumes (mL)		
	Ethyl ethanoate	Ethanoic acid	Water
7	25.00	0.00	0.90
8		2.00	2.40
9		4.00	4.00
10		6.00	7.00
11		8.00	10.60
12		10.00	16.40
13		12.00	23.80

2.2 Tie-lines obtention

Four mixtures (A, B, C, and D) were prepared using the volumes of water, ethanoic acid, and ethyl ethanoate described in Table 3. The preparation of each them was realized with magnetic agitation for 10 minutes at room temperature (298.15 K). Then, each mixture was submitted to one stage of extraction, compound by contact and separation. The ternary systems were made in contact by vigorous agitation in a separation funnel of 60.0 mL and were kept in repose for 5 minutes. The aqueous and organic phases were separated for a posterior measure of mass and volume. Aliquots of 5.00 mL of each phase were titrated with sodium hydroxide solution (NaOH) 1 mol L⁻¹ using 3,3-bis(4-hydroxyphenyl)-2-benzofuran-1-one ($C_{20}H_{14}O_4$) as the indicator.

The volumes of NaOH expended in each titration were presented in Table 4.

Table 3. Data survey for tie-lines obtention.

Component	Volumes of the mixtures (mL)			
	A	B	C	D
Ethyl ethanoate	25.00	25.00	25.00	25.00
Ethanoic acid	8.00	5.00	2.00	4.00
Water	17.00	20.00	23.00	21.00

Table 4. Titration data of the mixtures A, B, C, and D at T = 298.15 K under P = 101325 Pa.

Mixture	Aqueous phase				Organic phase			
	volume (mL)	mass (g)	volume NaOH (mL)	mols NaOH/10 ⁻³ (5 mL)	volume (mL)	mass (g)	volume NaOH (mL)	mols NaOH/10 ⁻³ (5 mL)
A	17.00	15.79	14.30	14.30	33.00	30.47	14.40	14.40
B	21.50	21.02	9.40	9.40	25.00	23.08	9.10	9.10
C	25.00	24.26	3.60	3.60	25.00	23.07	3.30	3.30
D	25.00	22.47	7.73	7.73	26.00	24.05	7.00	7.00

2.3 Plotting the equilibrium data

The ternary phase diagram of water/ethanoic acid/ethyl ethanoate system was built using the Origin[®] software from of equilibrium data obtained in items 2.1 and 2.2. The volumes were converted in mass using the densities of each component at 298.15 K ($\rho_{\text{ethanoic acid}} = 1.052 \text{ g mL}^{-1}$; $\rho_{\text{ethyl ethanoate}} = 0.901 \text{ g mL}^{-1}$; and $\rho_{\text{water}} = 0.997 \text{ g mL}^{-1}$). The diagram was used to study the liquid-liquid extraction process of ethanoic acid (C₂H₄O₂) from aqueous phase with the use of ethyl ethanoate as the solvent.

3. Results and discussion

The equilibrium compositions in the binodal curve (in mass fraction) for each component of the water/ethanoic acid/ethyl ethanoate system at 298.15 K and 101325 Pa were given in Table 5. The same results were plotted in Figure 1. The area of the biphasic liquid region obtained results from the mutual solubility of the solute (ethanoic acid) in the aqueous and organic solvent (ethyl ethanoate).

Table 5. Mass fractions of the compounds of the ternary system at T = 298.15 K under P = 101325 Pa.

Phase	Binodal curve point	Water	Ethyl ethanoate	Ethanoic acid
Water-rich	1	0.9171	0.0829	0
	2	0.8258	0.1045	0.0697
	3	0.7510	0.1222	0.1268
	4	0.6639	0.1680	0.1681
	5	0.5836	0.2194	0.1970
	6	0.5008	0.2878	0.2114
Ethyl ethanoate-rich	7	0.4030	0.3826	0.2144
	8	0.3310	0.4560	0.2130
	9	0.2546	0.5427	0.2028
	10	0.1949	0.6289	0.1762
	11	0.1298	0.7332	0.1370
	12	0.0886	0.8336	0.0779
	13	0.0383	0.9617	0

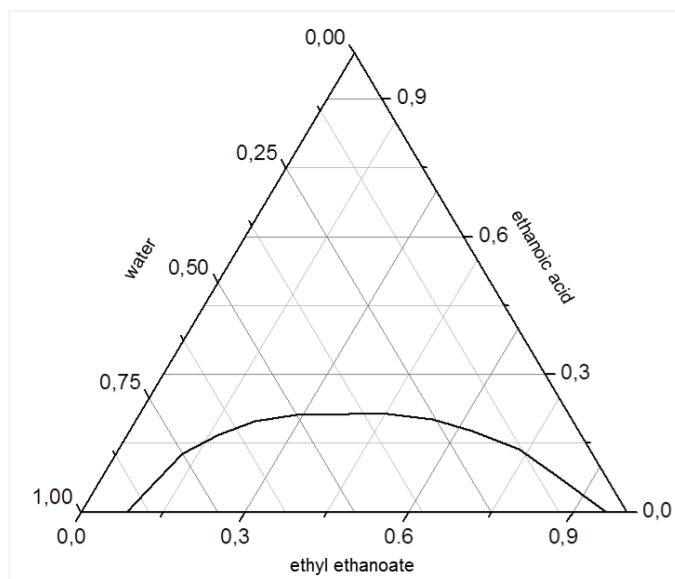


Figure 1. Ternary phase diagram of water/ethanoic acid/ethyl ethanoate system with binodal curve at $T = 298.15$ K under $P = 101325$ Pa.

The titration reaction involved in the volumetric analysis of ethanoic acid determination in each of the phases of the mixtures A, B, C, and D was presented in Equation 1. Since the reaction is 1:1, at the point of equivalence, the molar amount of ethanoic acid was equal to the sodium hydroxide. The formation of the reaction product, the acetate conjugate base (CH_3COO^-), was easily identified by the use of the indicator 3,3-bis (4-hydroxyphenyl)-2-benzofuran-1-one ($\text{C}_{20}\text{H}_{14}\text{O}_4$), which has a transition zone in the alkaline region.



The mass fractions of ethanoic acid (MW $60.052 \text{ g mol}^{-1}$), calculated from the equivalence of the number of moles of sodium hydroxide, as well as the mass fractions for the other components of the ternary system, found directly in the obtained diagram, were given in Table 6. The results obtained were plotted in Figure 2, where the tie-lines of each mixture were drawn.

Table 6. Mass fractions of the tie-lines of the ternary system at $T = 298.15$ K under $P = 101325$ Pa.

Mixture	Aqueous phase			Organic phase		
	Ethanoic acid	Water	Ethyl ethanoate	Ethanoic acid	Water	Ethyl ethanoate
A	0.1849	0.6253	0.1905	0.0965	0.0978	0.8055
B	0.1155	0.7652	0.1201	0.1018	0.1026	0.7928
C	0.0446	0.8558	0.0973	0.0430	0.0680	0.8890
D	0.1033	0.7849	0.1126	0.0874	0.0907	0.8225

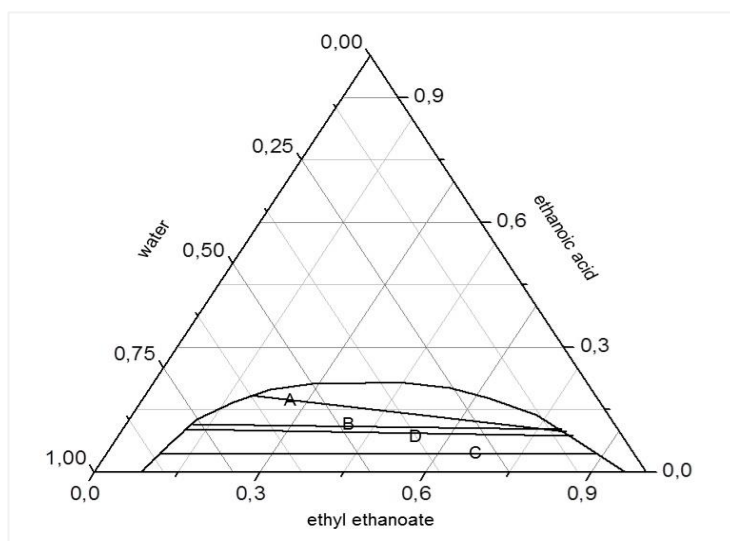


Figure 2. Ternary phase diagram of water/ethanoic acid/ethyl ethanoate system with the tie-lines corresponding to mixtures A, B, C, and D at $T = 298.15$ K under $P = 101325$ Pa.

The results obtained in the study of liquid-liquid extraction for the water/ethyl ethanoate/ethanoic acid ternary system were summarized in Figure 3. The ethyl ethanoate free-base feed composition was represented by F point (water/ethanoic acid/ethyl ethanoate = 0.84/0.16/0) and extractor solvent (pure) was represented by B point (water/ethanoic acid/ethyl ethanoate = 0/0/1). The intersection between the FB segment and the tie-line corresponding to the D mixture was represented by the M point, which in turn binds the extract (E) and residue (R) phases in equilibrium in the binodal curve. The equilibrium composition of the E and R phases in the mass fraction of ethanoic acid was of $Y_e = 0.098$ and $X_r = 0.102$, respectively.

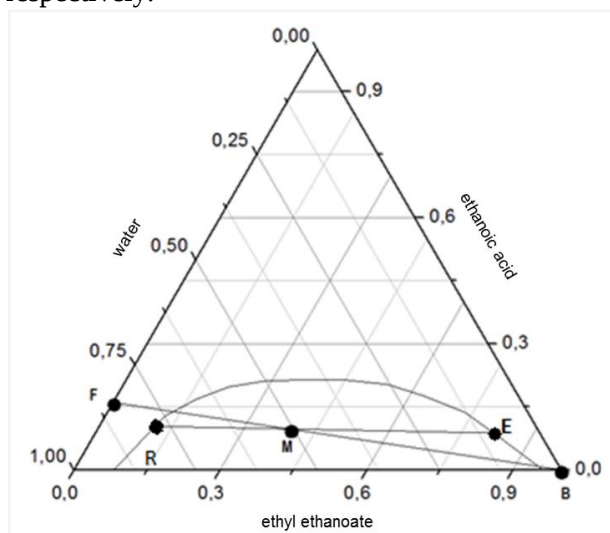


Figure 3. Ternary phase diagram of water/ethanoic acid/ethyl ethanoate system for mixture D at $T = 298.15$ K under $P = 101325$ Pa (where F: feed; B: solvent; M: F + B mixture; E: extract, and R: residue).

The distribution coefficients (D) and the separation factors (S) for mixtures A, B, C, and D were calculated to evaluate the efficacy of extraction of ethanoic acid by the organic solvent (ethyl ethanoate) by Equation 2. The separation factor, which is a measure of the ability of a solvent to separate a solute from water, was defined as the ratio between the ethanoic acid (D_2) and water (D_1) distribution coefficients, respectively. The experimental values of the distribution coefficients and separation factors, for each mixture of the ternary system, were listed in Table 7.

$$S = \frac{D_2}{D_1} = \frac{x_{EA,EE}/x_{EA,W}}{x_{W,EE}/x_{W,W}} \quad (2)$$

where:

S = separation factor;

D_1 = distribution coefficients for water;

D_2 = distribution coefficient for ethanoic acid;

$x_{EA,EE}$ = mass fraction of ethanoic acid in the ethyl ethanoate-rich phase;

$x_{EA,W}$ = mass fraction of ethanoic acid in the water-rich phase;

$x_{W,EE}$ = mass fraction of water in the ethyl ethanoate-rich phase;

$x_{W,W}$ = mass fraction of water in the water-rich phase.

Table 7. Distribution coefficients for water (D_1) and ethanoic acid (D_2) and separation factors (S) at $T = 298.15$ K under $P = 101325$ Pa.

System	Mixture	D_1	D_2	S
Water +	A	0.16	0.52	3.34
Ethanoic	B	0.13	0.88	6.57
acid +	C	0.08	0.96	12.13
Ethyl	D	0.12	0.85	7.32
ethanoate				

The organic solvent chosen was found to have shown satisfactory separation factors (i.e. > 1), indicating its ability to extract ethanoic acid from water. The results demonstrated that the separation factor decreases in the order of the mixtures $C > D > B > A$. For the ternary system, increasing the ethanoic acid content in the mixtures decreased the separating ability of ethyl ethanoate. The ethanoic acid distribution coefficients showed values higher than the water distribution coefficients, suggesting a higher preference of the solute to be distributed in the organic phase than in the aqueous phase.

The percentages liquid-liquid extraction (%LLE) of ethanoic acid in water were determined for each mixture by tie-lines method and Equation 3 and can be checked in Table 8. The results suggested that the percentage extraction decreases in the order of the mixtures $D > B > C > A$, indicating that, for concentrations of ethanoic acid greater than 16% in F, there was a reduction in the solvent extraction capacity. In short, ethyl ethanoate showed good performance in extracting ethanoic acid from the aqueous phase of the mixtures.

$$\%LLE = \left(\frac{x_F^F - x_R^R}{x_F^F} \right) \times 100 \quad (3)$$

where:

x_F = feed mass fraction;

x_R = residue mass fraction;

F = feed mass;

R = residue mass.

Table 8. Percentage liquid-liquid extraction (%LLE) of ethanoic acid in the mixtures A, B, C, and D

Mixture	x_F	x_M	x_R	y_E	F	M	R	E	%LLE
A	0.3318	0.1757	0.1849	0.0965	25.3650	47.8900	42.9255	4.9645	5.69
B	0.2087	0.1102	0.1155	0.1018	25.2000	47.7250	29.3135	18.4115	35.63
C	0.0840	0.0442	0.0446	0.0430	25.0350	47.5600	36.8250	10.7350	21.94
D	0.1673	0.0883	0.1033	0.0874	25.1450	47.6700	2.6190	45.0510	93.57

In practice, it is believed that for mixtures with higher solute contents, the desired extraction percentage can be achieved by adopting mass transfer optimization strategies. Among them: an increase in the number of stages (contact and separation); an increase in the driving force of the process; favoring the flow of material of interest; increase in a concentration gradient etc.

4. Conclusions

The application of construction of a ternary phase diagram in the study the liquid-liquid extraction of the water/ethanoic acid/ethyl ethanoate system was quite satisfactory. The obtention of the equilibrium data of the ternary system made it possible an evaluation of the distribution and of the mutual solubility of the solute in the aqueous and organic phases. The determination of the composition of the extract and residue portions in the equilibrium of each mixture by of the tie-lines method allowed to examine the percentages of liquid-liquid extraction achieved by ethyl ethanoate. The acting of the solvent was evaluated by calculations of separation factors and percentage extraction, showing its good performance as an extractor solvent of ethanoic acid in the aqueous phase at room temperature and atmospheric pressure.

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