SYNERGISTIC EXTRACTION OF ACETIC ACID
FROM ITS AQUEOUS SOLUTION

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ABSTRACT

Liquid-liquid extraction is the one of the simplest and cost effective separation method. In this work the extraction of acetic acid from aqueous solution by using ethyl acetate and MIBK as individual and also as a mixed solvent were carried out to study the liquid-liquid equilibrium. The different feed concentrations of acetic acid were studied with various combinations of mixed solvent. The result shows that the high synergisms were obtained for mixed solvent and higher concentration of feed gives the best result. GCEOS and PRSV models available in HYSIS simulation software were used to calculate the K_d values and these values were compared with experiment results to select the best model.
Keywords: liquid-liquid extraction, acetic acid, solvent, ternary diagram, HYSIS, simulation.

INTRODUCTION

In separation and purification technology the liquid-liquid extraction plays an important role. The liquid-liquid extraction is used to separate two miscible liquids using a solvent that preferentially dissolves one of them [1]. The three branches of solvent extraction are the traditional applied field, the nuclear material field and the theoretical field [2]. This is a low temperature and a low cost process. Metals are also purified by this process. Close boiling mixtures or substances can also be separated by this method [3]. The equilibrium relationship of the components involved is of prime importance in solvent extraction. The equilibrium relationship in liquid extraction are generally more complicated than for other separations, because there are three or more components present in each phase. So, the equilibrium relationships are presented on a triangular diagram [3]. The effect of dual solvent was found to bring synergism, when compared to the single solvent, the reciprocal property also satisfied with the dual solvent extraction. In simulation methods the UNIFAC, UNIQUAC models are usually studied, but these are based on temperature parameter [3]. For hydrocarbon feed the PRSV, GCEOS models are preferred.

Acetic acid is one of the most widely used carboxylic acids. It is used in many reactions, for example, the synthesis of acetic ester or it can be used as a solvent. The separation of acetic acid from its aqueous solution by simple rectification is very difficult, requiring a column with many stages and a high reflux ratio, thus incurring high running costs [4]. In practice other processes are also used depending on the concentration of acetic acid present in the feed. Between 50 % and 70 % w/w acetic acid, extractive distillation is used. By adding a third component, the volatility of water is increased

and the separation can be achieved with less energy [4]. Below 40 % acetic acid, liquid-liquid extraction with single solvent is the most appropriate. Acetic acid is extracted from water by a suitable solvent in order to obtain substantially pure acetic acid [4].

The choice of a suitable extracting solvent for any liquid extraction duty mainly depends on its extractive capacity and equilibrium characteristics apart from its stability, favorable density, viscosity and interfacial tension properties and sufficient difference in boiling point between the solute and the solvent [5]. For the feed containing 50 % of acetic acid, MIBK is the most widely used solvent [4].

The solubility is less for MIBK when compared to ethyl acetate. On the other hand the boiling point of the MIBK is close to the boiling point of the acetic acid. So the separation is difficult. The combined action can bring out synergism, due to the increased solubility of the solute in the mixed solvent.

EXPERIMENTAL

The simple mixer – settler described elsewhere [6] is used to study the equilibrium and 50 %, 40 %, 30 % and 20 % ($\%_{mass}$) of acetic acid samples were prepared by adding the acid in the water and these samples were used to carry out liquid - liquid extraction studies using ethyl acetate, MIBK and the combination of these two solvents. The feed and solvent mixture were mixed for 15 min and allowed to settle for 15 min and these timings were fixed by trial runs. The extract (bottom) phase was analyzed by acid-base titration method and the raffinate (top) phase was analyzed by spectrophotometer. The experiments were carried out at room temperature and pressure.

RESULTS AND DISCUSSION

For the feed containing 20 % of acetic acid, the separation from aqueous solution with various solvents has been reviewed using reported distribution coefficient values and distribution coefficients obtained in the present experimental work. Analysis of distribution coefficient values for various solvents and feed containing 20 % acetic acid shows that ethyl acetate gives better extraction result than MIBK and their combination

Table 1. Distribution coefficients for feed containing 20 % of acetic acid.

Solvents	Distribution coefficient (K_d)	Reference
Ethyl acetate	24.2	Present work
MIBK	7.235	Present work
n-Butanol	16.37	Present work & Fahim [3]
Ethyl ether	6.179	Present work & Judson [5]
Cyclohexyl acetate	3.880	Tamura [8]
Cyclohexanol	11.48	Matsumoto [9]
1-Hexanol	6.29	Fahim [3]
Cyclohexanol+ Cyclohexyl acetate	8.125	Cehreli [9]
Hexane	6.29	Present work
Tri-n-octylamine	2.34	Michiaki [10]

which is also observed from Table 1. Analysis of the experimental distribution coefficients obtained for various feed concentrations (20 %, 30 %, 40 % and 50 %) and different solvent ratios in Table 2 shows that for feed containing lower concentration of acetic acid, ethyl acetate alone is suitable. It is also observed from the K_d values that for the feed containing higher concentrations of ethyl acetate (50 %) is not able to give any result and this due to the co-extract, the water from the solvent [6]. Whereas for the feed containing higher concentration (40 %, 50 %) of acetic acid, combination of these solvents exhibits synergism. Increase in the value of distribution coefficient in this case is due to the favoured conditions arising from the combined action. The increase in distribution coefficient for the case of mixed solvent (Ethyl Acetate + MIBK) is being explained using ternary diagram drawn below.

Ternary equilibrium diagram for single solvent

From the literature the equilibrium diagram for the ternary systems ethyl acetate/acetic acid/water and MIBK/acetic acid/water were taken [4], and shown in Fig. 1a, 1b. The two phase region is quite small for ethyl acetate/acetic acid/water shown in Fig. 1a, limiting the maximum feed concentration for the liquid-liquid extraction. However, the two phase region for the ternary system MIBK/acetic acid/water is larger (Fig.

Table 2. Comparison of distribution coefficients for various feed concentrations.

Sample No	Solventt ratio (s)	Distribution coefficient(K_d)			
		20 %	30 %	40 %	50 %
1	0(Ethyl acetate)	24.2	2.35	-	-
2	0.1	16.1	1.23	4.81	54.2
3	0.2	-	1.49	2.18	3.73
4	0.3	-	-	9.27	9.272
5	0.4	19.3	1.52	4.94	58.89
6	0.5	12.7	12.4	-	-
7	0.6	14.0	-	56.4	-
8	0.7	-	1.72	3.07	-
9	0.8	8.81	2.6	3.42	5.516
10	0.9	2.53	4.23	-	7.89
11	1	7.23	6.52	4.53	3.63

Table 3. Comparison of estimated distribution coefficients with experimental values (for feed concentration of 50 %).

Solvent ratio (s)	Distribution Coefficients (K_d)		
	Experiment results	GCEOS model	PR model
0 (Ethyl acetate)	-	-	-
0.1	3.63	1.6	1.021
0.2	-	12.74	1.6
0.3	4.56	2.53	1.013
0.4	5.516	8.816	1.017
0.5	-	15.54	1.036
0.6	-	14.05	1.017
0.7	58.89	19.37	1.021
0.8	9.272	22.25	1.046
0.9	3.73	-	1.718
1(MIBK)	54.2	16.11	1.148

1b) and therefore can be used for higher feed concentrations. Similar binodal curve for the ternary system of acetic acid/water/ethyl acetate + MIBK have been drawn using the calculated tie line data from the present experimental work [11] and shown in Fig. 2. It is observed that the two phase region is higher than that for the single solvent system (ethyl acetate as well as MIBK).

Model predictions and comparison

GCEOS and PRSV models in HYSIS simulation software were used to find the distribution coefficients (K_d) for the feed concentration of 50 % and mixed solvents. The calculated K_d values were compared with experimental results in Table 3 and the % RMSD (Root Mean Square Deviation) are 26 % and 90 % for GCEOS and PRSV models, respectively. This shows that GCEOS can predict the results which are in good comparison with the experimental results.

CONCLUSIONS

Effect of dual solvent on liquid-liquid equilibrium has been analyzed in terms of distribution coefficients and ternary diagram and the suitable models for estimating the distribution coefficients discussed. The distribution coefficients for various acetic acid feed concentrations were studied using different combination of solvent. The liquid-liquid equilibrium was drawn in the
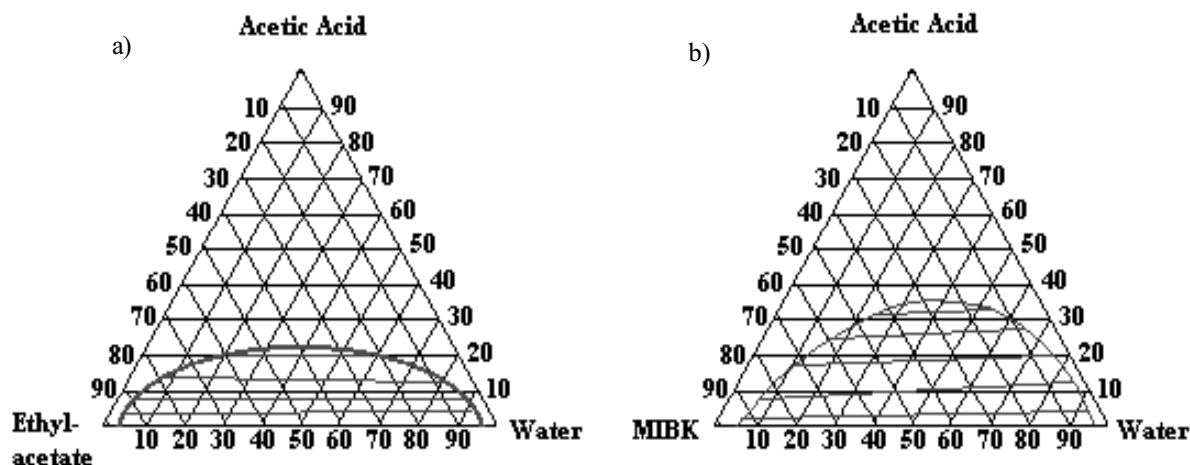

Fig. 1. Ternary equilibrium diagram for single solvent: 1a. Ternary equilibrium diagram for ethyl acetate/acetic acid/water; 1b. Ternary equilibrium diagram for MIBK/acetic acid/water.
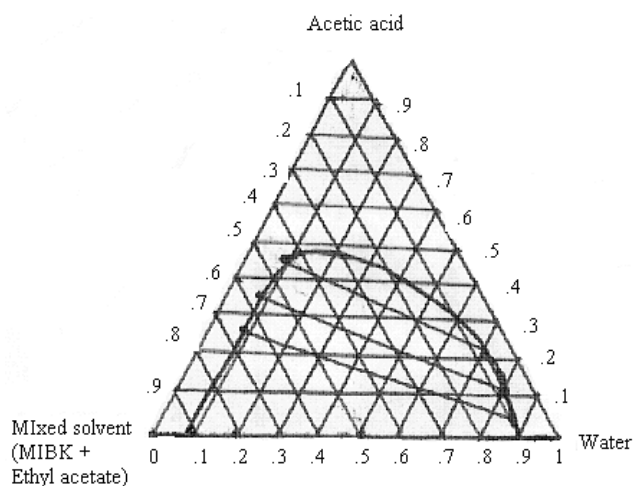
Fig. 2. Ternary equilibrium diagram for a system of acetic acid/water/ethyl acetate + MIBK.

form of ternary graph for the feed containing 50 % acetic acid. The distribution coefficient data were obtained using models available in HYSIS software and GCEOS model could predict the values with less RMSD when compared with PRSV model. Though it could appreciate the effect of dual solvent on improving the extraction efficiency, as an extension of this work, further investigations can be done because the effect of property change and temperature on mixing have not been taken into consideration. However, this study would definitely give a first hand knowledge about the problem and pro-

vide a good insight into the complex and conflicting of the parameters governing the process.

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