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INFLUENCE OF TEMPERATURE AND ESTIMATION OF ENTHALPY AND ENTROPY FOR REACTIVE EXTRACTION OF LACTIC ACID

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ABSTRACT

This paper deals with lactic acid extraction by using tri-n-butyl phosphate (TBP) extractant dissolved in diluents (Methyl ether diketone (MIBK), 1-dedocanol & di ethyl ether) at different temperatures range (298, 313, 323, 333 K). Chemical equilibrium experiments have been carried out to investigate the effect of temperature on the extraction efficiency of tri-n-butyl phosphate (TBP) as well as on the equilibrium extraction constant. It was found that distribution coefficient ($K_{D)}$ decreased with increasing the temperature. However, an improved separation of the phases is observed. The extraction equilibrium constants have been determined using a mathematical model of reactive extraction. The apparent enthalpy and entropy of the reactive extraction with systems (TBP/MIBK, TBP/1-dedocanol TBP/di ethyl ether) are also determined.

Key words: Lactic acid, Reactive extraction, Tri-n-Butyl phosphate (TBP), Diluents, Extraction efficiency, Temperature.

INTRODUCTION

Lactic acid or 2-hydroxypropanoic acid is a carboxylic acid that contains both hydroxyl and carboxyl group in its molecule. The acid is widely used in food, chemical and pharmaceutical industries. It also has been used in production of polylactate, a biodegradable polymeric material. As a result, high purity lactic acid has been constantly in high demand. Lactic acid can be produced by either chemical synthesis or by fermentation[1,2].

Reactive extraction of lactic acid from dilute solutions (fermentation broth and wastewater) involves use of an extractant-diluent system to extract acid[3-5].

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Organophosphorous compounds are effective extractants and provide higher distribution coefficients than that of carbon bonded oxygen bearing extractants[6]. The chemical stability of organophosphorous compounds plays an important role in the possibility of its use as an efficient extractant with good separation efficiency. TBP, an organophosphorous compound, contains a phosphoryl group (>P = O) which serves as a stronger Lewis base for its high polarity. This leads to a high degree of extraction. TBP is selected because of its low water co-extraction (4.67% by weight at $20^{o}C$) and very low solubility in the aqueous phase (0.04% by weight at $20^{o}C$)[6-9].

In this equilibrium study, a different diluents such as MIBL, 1-dodecanol, di ethyl ether and di iso propyl ether are used to provide the appropriate physical properties of extractant (TBP) and improved extraction efficiency[7].

Diluent is usually added along with the extractant to enhance its physical properties by providing general solvation and affect the extraction power of the extractant by providing specific inter-action. The diluent may consists of one or more components, inert or active. Various active polar and proton or electron donating diluents (halogenated aliphatic/aromatic hydrocarbons, ketones, nitrobenzenes, higher alcohols), enhance the extraction. On the other hand, inert diluents (long chain paraffins, benzene etc.), limit the solvent capacity[10]. Equilibrium extraction constant (K_E) are determined with mathematical model using experimental data. The results of equilibrium experimental study are useful to design extraction processes for recovery of lactic acid from the fermentation broths.

Theory

The extraction process is analyzed by means of the degree of extraction and distribution coefficient. The distribution coefficient, K_D, is calculated using Eq. 1.

$$K_D = \frac{[LA]_{org}}{[LA]_{aq.}} \qquad \ldots(1)$$

where, $[LA]_{org.}$ is the total acid concentration (dissociated and un-dissociated) in aqueous phase at equilibrium and $[LA]_{aq.}$ is the total concentration of lactic acid in organic phase. The degree of extraction is defined as the ratio of acid concentration in the extracted phase to the initial acid concentration in aqueous solution by assuming no change in volume at equilibrium as given by Eq. 2.

$$E = \frac{K_D}{K_D + 1} \times 100\,\% \qquad \ldots(2)$$

The extent to which the organic phase (extractant and diluents) may be loaded with acid is expressed by the loading ratio, Z (ratio of total acid concentration in the organic phase to the total extractant concentration) as given by Eq. (3).

$$Z = \frac{[LA]_{org}}{S} \qquad \ldots(3)$$

The value of Z depends on the extractability of the acid (strength of the acid base interaction) and its aqueous concentration. The stoichiometry of the overall extraction equilibrium depends on the loading ratio in organic phase (Z). If the organic phase is not highly concentrated by acid, i.e., at very low loading ratios ($Z < 0.5$), 1 : 1 complex of acid and extractant is formed. A plot of Z/(1-Z) versus $[LA]_{aq.}$ yields a straight line passing through origin with a slope of complexation constant (K_{E1}) as given by Eq. (4):

$$\frac{1 \quad Z}{1+Z} = K_{E1}\,[LA]_{aq.} \qquad \ldots(4)$$

For higher loading ratios (at least, $Z > 0.5$):

$$\frac{Z}{2+Z} = K_{21}\,[LA]^2{}_{aq.} \qquad \ldots(5)$$

The values of equilibrium constants (K_{E1}) for the formation of 1 : 1 complexes are estimated using Eqs. (5) by plotting Z/(2 – Z) vs. $[LA]^2{}_{aq}$.

EXPERIMENTAL

Materials and methods

Materials

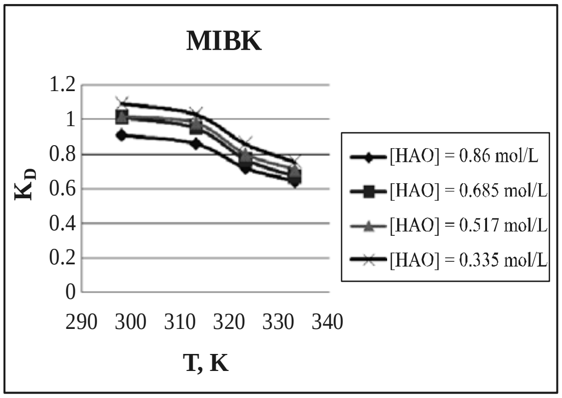
Tri-*n*-butyl phosphate, used as extractant and iso propyl ketone (MIBK), 1-dedocanol and di ethyl ether used as diluents. All compounds are used without any pretreatment. Aqueous solutions of lactic acid are prepared using de-ionized water. NaOH used for titration and phenolphthalein solution (pH range 8.2-10.0) was used as an indicator for titration.

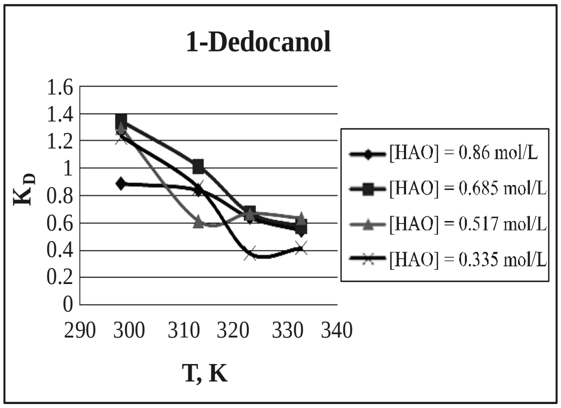
Methods

The extraction equilibrium experiments are carried out at four different constant temperatures (298, 313, 323 and 333 K) with equal volumes (20 cm^3 of each phase) of the aqueous and organic solutions mixed in conical flasks of 100 mL and shake them for 2 hrs. After attaining equilibrium, both the phases are separated in centrifuge at speed 1400 rpm for 30 min. After separation, the aqueous phase is analyzed to determine the concentration of acid by titration using fresh 0.02 N NaOH solution and phenolphthalein as an indicator. The acid concentration in the organic phase is calculated by mass balance. repeat the same procedure with 1-dedocanol and diethyl ether at different temperatures.

RESULTS AND DISCUSSION

Since TBP has a relatively high viscosity (3.56 x 10^{-3} Pa s) and density close to unity (0.98 g cm^{-3}), it is used along with diluents, which could facilitate good phase separation in the continuous extraction process. Diluents chosen in the study are MIBK, 1-dedocanol and diethyl ether. When TBP was used as an extractant in a mixture with diluent, then the solubility of extracted species increased in the organic phase. So, it was observed from experiment runs that degree of extraction decreases with increasing the temperature of the system. The results of the reactive extraction of lactic acid by using tri butyl phosphate dissolved in different diluents such as MIBK, 1-dedocanol and diethyl ether is listed in Fig. 1.


MIBK


1-Dedocanol

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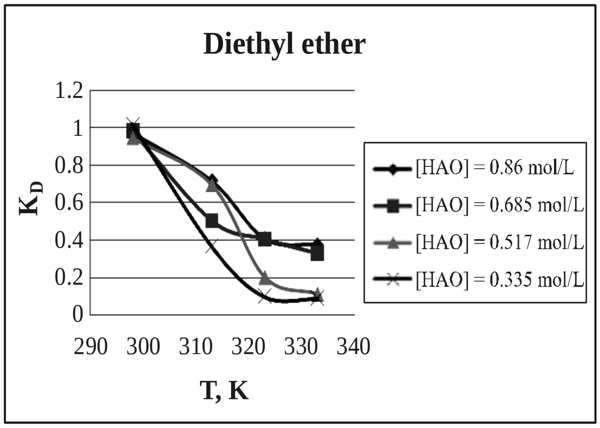

Fig. 1: Effect of temperature on distribution coefficient

Effect of temperature

From the results that listed in Table 1, we see that increase in temperature led to decrease in the degree of extraction and distribution coefficient and K_{E1}. For the concentration range of lactic acid, the increase in the thermal energy disturbs the interaction in the organic phase between TBP and acid, thus decreasing the extraction. However, an improved separation of the phases was observed. The temperature is maintained constant at four different values (298, 313, 323 and 333 K).

From a thermodynamic point of view the molecules of acid in the organic phase are more ordered as they appear as a complex. Thus, acid transfer from the aqueous phase as solvates to the organic phase increases the order and reduces entropy. Generally the transfer of compounds from the aqueous phase to the organic phase is accompanied by a decrease in entropy. If the enthalpy and the entropy of this reaction assumed to be constant over the temperature range, these can be estimated using Van't Hoff Equation (Eq. 6).

$$\text{Ln } K_E = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \ldots(6)$$

The slope and intercept of a plot of ln K_E vs. 1/T give the apparent enthalpy and entropy of reactive extraction reaction respectively as shown in Fig. 2. Table 1 indicates the results that obtained from Fig. 1 for the enthalpy and entropy for reactive extraction of lactic acid by using tributyl phosphate dissolved in different diluents.

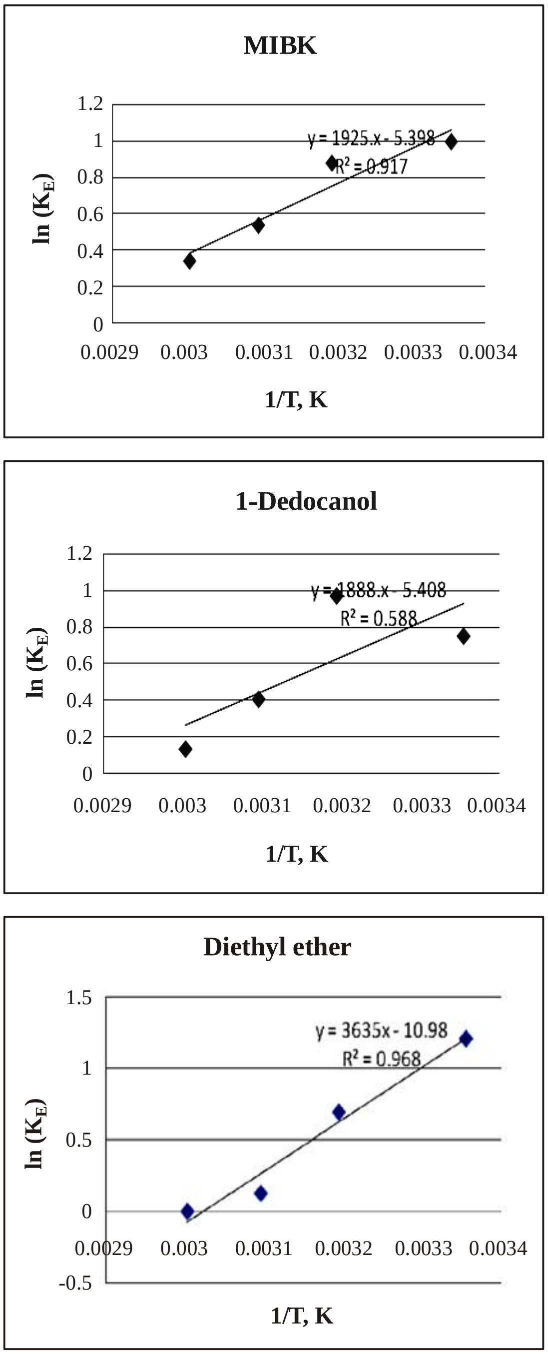

Fig. 2: Determination of apparent enthalpy and entropy of reaction for the extraction of lactic acid with TBP (0.5 Kmol m^{-3}) diluted in MIBK, 1-dedocanol and di ethyl ether

Table 1: Enthalpy and entropy at different diluents

Diluents	Enthalpy (KJ. Mol^{-1})	Entropy (J mol^{-1} K^{-1})
MIBK	-1.925	- 44.87
1-dedocanol	- 1.888	- 44.962
Diethyl ether	- 3.635	- 91.287

CONCLUSION

Different parameters like distribution coefficient, degree of extraction, and equilibrium complexation constants are determined. The increase in temperature in the range of 298-333 K affects the extraction equilibrium significantly. As the temperature increases, the percentage amount of acid extracted is found to decrease and degree of extraction decrease and K_{E1}. The enthalpy and entropy of reactive extraction are found to be -1.925 KJ mol^{-1} and -44.87 Jmol^{-1} K^{-1} by using MIBK as diluents, -1.888 KJ mol^{-1} and -44.962 Jmol^{-1} K^{-1} by using 1-dedocanol as diluent and -3.635 KJ mol^{-1} and -91.287 Jmol^{-1} K^{-1} by using diethyl ether as diluents respectively where the negative sign of the enthalpy is mean that the reaction between the lactic acid and the organic phase (extractant and diluents) is exothermic.

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