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Investigation of Diluting Solvent Effects on the Extraction of Glycolic Acid with Tri-n-octylamine

Ismail Inci
Department of Chemical Engineering, Faculty of Engineering,
Istanbul University 34850, Avcilar, Istanbul, Turkey

Abstract: The purpose of this study is to investigate the effect of solvent types on the extraction of glycolic acid, an important biotechnological product, from aqueous solutions with tri-n-octylamine. The extractant tri-n-octylamine used here is a long chain tertiary amine. Diluting solvents used in this study are heptane, hexane, cyclohexane, isooctane, toluene and methylisobutylketone (MIBK). Furthermore toluene - MIBK mixture was used too in 1:1 volume ratio. The distribution coefficients and loading factors were calculated from experimental results and compared with each other. Among the diluents used in this study, the best results were obtained with MIBK.

Key words: Glycolic acid, Extraction, Distribution Coefficient, tri-n-octylamine

Introduction

Glycolic acid is also known as hydroxyacetic acid. Hydroxyacetic acid occurs in nature in sugar beets, unripe grapes and spent sulphite liqueor from pulp processing. However, it has never been produced commercially from these sources. The acid was available before 1940 only in limited quantities, and was prepared from the hydrolysis of monohalogenated acetic acids. It may have been produced in Germany at one time by the electrolytic reduction of oxalic acid. Hydroxyacetic acid is produced commercially in the United States as an intermediate in the manufacture of ethylene glycol.

Hydroxyacetic acid is produced in large volume. Nevertheless, it has found uses in a number of areas, e.g, adhesives, metal cleaning, electroplating , dairy product cleaning, biodegradable polymers, dyeing, water well cleaning, textiles and detergents. Numerous properties of hydroxyacetic acid contribute to its diversified use in cleaning dairy and food processing equipment. In common with some other hydroxy organic acids, hydroxy acetic acid reacts with copper oxide to form a complex salt. This property has been utilized in the bright dipping of copper before drawing it into wire (Kirk - Othmer 1981). The extract ability of most carboxylic acids by current solvents is very low, and reactive extraction must be considered. High molecular amines seem to be promising extractants for this purpose (Bizek *et al.* 1992).

Long chain aliphatic tertiary amines with seven to nine carbon atoms in each alkyl group are effective extractants for carboxylic acids (Kertes and King,1986). Amines are used with suitable organic diluents, and these diluents may modify the extraction power of the amines .

In this work, the extraction of glycolic acid, which is an important biotechnological product, with tri-n-octylamine in different solvents at constant temperature has been investigated.

Materials and Methods

In the design of the extraction process, distribution coefficient is an important parameter. Distribution coefficient is calculated as fallows.

$$D = \frac{[\text{Acid equivalent / unit organic phase}]}{[\text{Acid equivalent / unit aqueous phase}]} \quad (1)$$

Recently, Z , loading factor is used for presenting the extraction efficiency (Tamada and King 1990).

In amine extraction of carboxylic acids Z is defined as:

$$Z = \frac{m_a}{m_e} \quad (2)$$

where,

m_a = Concentration of glycolic acid in organic phase

m_e = Concentrationf amine in organic phase Tri-n-octylamine used as liquid extractant is a commercial product produced by Merck Co. It was used as received. Glycolic acid (Merck Co.) as well as other reagents used were of analytical grade.

Aqueous glycolic acid solution (% 10 w) was prepared using distilled water. Organic phase was prepared by mixing solvents (heptane, hexane, cyclohexane, isooctane, toluene and methylisobutylketone) with tri-n-octylamine in 5 different concentrations. Initial concentrations of tri-n-octylamine in organic phase are 1.80 mol/L, 1.40 mol/L , 1.10 mol/L, 0.70 mol/L , 0.40 mol/L. The extraction was performed by shaking equal volumes of initial aqueous and organic phases in a thermostated bath for 2 h. Thereafter the mixture was left for 6-8 h to reach full separation of phases. Experiments were carried out at 25±0.1 °C.

The equilibrium of acid concentrations were determined by volumetric titration with standardized 0.1 N NaOH.

Results and Discussion

Distribution coefficients and loading factors calculated from experimental results are presented in Table 1 and Figs. 1, 2 and 3. As can be seen from Figs. 1 and 2 the distribution coefficients increase with increasing tri-n-octylamine concentration for all diluents. The extraction efficiency of the diluents can be presented as follows:

MIBK > Toluene > Hexane > Isopoctane > Cyclohexane > Heptane

This behaviour can be expressed with formation of acid - amine complex . The interactions between the complex and diluent can be divided as "general solvation" and "specific interactions" of the diluent with the complex. Hexane, heptane, cyclohexane and isooctane being nonpolar, provide very little solvation of the polar complex. Toluene is an aromatic solvent and it produces slightly higher distribution coefficients, as a result of solvation due to interaction of the aromatic π electrons

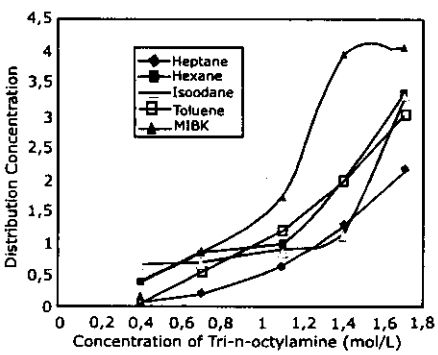

Fig. 1: Variation of Distribution Coefficients with Concentration of tri-n-octylamine in Different Diluting Solvents

Table I: Experimental Results of the Extraction of Glycolic Acid with tri-n-octylamine

Solvents	C_{TOA}) (mol / L	Z	D
Heptane	1.80	2,17	2,17
	1.40	1,28	1,28
	1.10	0,66	0,66
	0.70	0,22	0,22
	0.40	0,06	0,06
Hexane	1.80	3,36	3,36
	1.40	1,99	1,99
	1.10	1,01	1,01
	0.70	0,84	0,84
	0.40	0,39	0,39
Isooctane	1.80	3,34	3,34
	1.40	1,18	1,18
	1.10	0,91	0,91
	0.70	0,71	0,71
	0.40	0,67	0,67
Cyclohexane	1.80	2,92	2,92
	1.40	1,72	1,72
	1.10	0,84	0,84
	0.70	0,74	0,74
	0.40	0,31	0,31
Toluene	1.80	3,04	3,04
	1.40	1,97	1,97
	1.10	1,20	1,20
	0.70	0,40	0,40
	0.40	0,05	0,05
MIBK	1.80	4,04	4,04
	1.40	3,93	3,93
	1.10	1,73	1,73
	0.70	0,70	0,70
	0.40	0,60	0,60
MIBK + Toluene	1.80	0,74	8,45
	1.40	0,81	4,09
	1.10	0,69	1,81
	0.70	0,65	0,52
	0.40	1,08	0,46

with the complex. MIBK is polar, and can promote extraction by providing a good solvating media for the ion pair (Tung and King 1994).

Symbols

C_{TOA}: Concentration of tri-n-octylamine, (mol / L).

D: Distribution Coefficient

Z: Loading Factor

MIBK : Methylisobutylketone

m_a: Total amount of acid in organic phase

m_e: Total amount of amine in organic phase

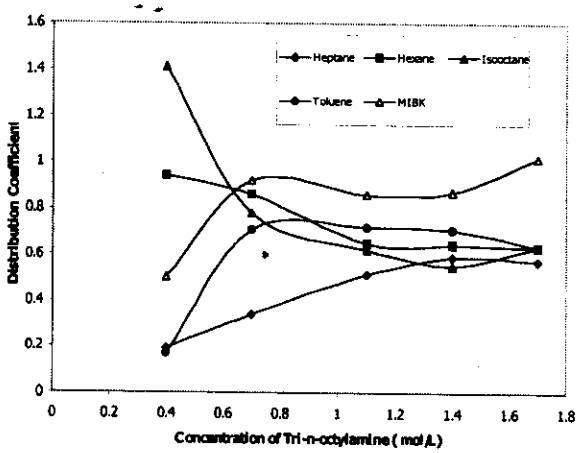

Fig. 2: Variation of Loading Factors with Concentration of tri-n-octylamine in Different Diluting Solvents

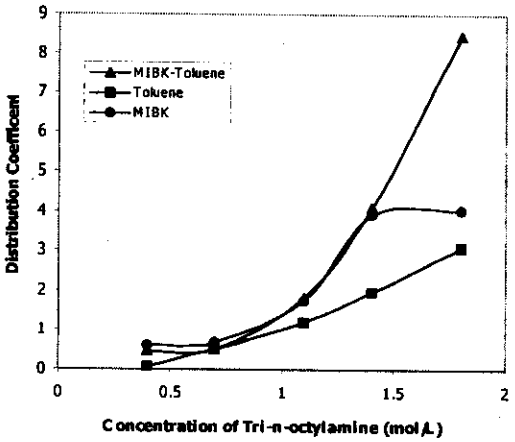

Fig. 3: Comparison of Toluene and MIBK Data with Toluene-MIBK Mixture

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