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Investigation of Diluting Solvent Effects on the Extraction of Tartaric Acid with Alamine-336

[1]Metin Hasdemir, [1]Mehmet Bilgin, [1]Ismail Inci and [2]Neşet Öztürk
[1]Istanbul University, Engineering Faculty, Department of Chemical Engineering
34850 Avcilar, Istanbul, Turkey
[2]Cekmece Nuclear Research Center, Istanbul, Turkey

Abstract: The goal of this study is to investigate the effect of solvent types on the extraction of tartaric acid, an important biotechnological product, from aqueous solutions with Alamine-336. The extractant Alamine-336 used here is a mixture of long chain tertiary amines. Diluting solvents used in this study are heptane, toluene, kerosene, methylisobuthylketone (MIBK) and isooctane. Furthermore toluene-kerosene 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 of diluents used in this study, the best results were obtained with MIBK.

Key words: Tartaric Acid, Extraction, Distribution Coefficient, Alamine-336

Introduction

The extraction of carboxylic acids from aqueous solutions and other broth has been investigated in connection with biotechnology boom in last decade. As shown by Kertes and King (1986), the extractability of most organic acids by current solvents is very low and reactive extraction must be considered (Kertes and King,1986). High molecular amines seem to be perspective extractants for this purpose (Bizek et. al.,1992).

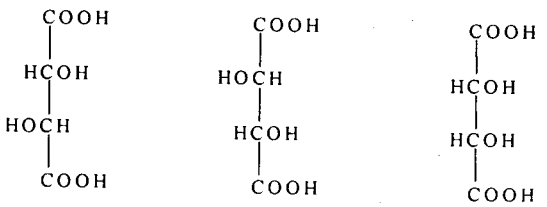
Long chain aliphatic tertiary amines with seven to nine carbon atoms in each alkyl group are effective extractants for carboxylic acids (Prochazka et. al., 1994). Amines are used with suitable organic diluents and these diluents may modify the extraction power of the amines (Tung and King 1994).

In this work, the extraction of tartaric acid, which is an important biotechnological product, with Alamine-336 in different solvents at constant temperature have been investigated.

Tartaric acid is the dextro form of 2,3 dihydroxysuccinic acid, $C_4H_6O_4$. It has been known since antiquity in the form of its acid potassium salt, which occurs in grapes. In the fermentation of grape juice to wine, the salt deposits in the fermentation vessels. The free crystallized tartaric acid was first obtained from such fermentation residues by Scheele in 1769. Tartaric acid can be obtained in four forms. The formulas (a) and (b) represent dextro-and levo tartaric acid, the prefixes referring to the direction of rotation of the plane of polarization of polarized light; (c) is meso-tartaric acid, which is inactive by "internal compensation".

In addition there is the racemic form, racemic acid, which is the equimoleculer mixture of (a) and (b) (Kirk-Othmer, 1981).

Tartaric acid is employed like citric acid in the preparation of carbonated drinks, especially grope flavored. It is widely used in effervescent tablets and powders, frequently admixed with citric acid. Tartaric acid is an acidulant in the manufacture of gelatin dessert and fruit jellies. It finds use in the cleaning and polishing of metals. In the textile industry it is used in calico printing for controlling the liberation of chlorine from



(a) (b) (c)

bleach powder. The acid is employed in certain types of photographic work for printing and developing (Kirk-Othmer, 1981).

Theoretical: Distribution coefficient that is an important parameter in the design of an extraction process, is calculated by equation (1).

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

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

Recently, z , loading factor is used for presenting the extraction efficiency (Prochazka et. al.1994, F. Emo *et al.* 1998). In amine extraction of carboxylic acids, where,

m_a = Total amount of acid in organic phase
m_e = Total amount of amine in organic phase

Experimental: Properties of chemical solvents used as diluent in this work were shown in Table1.

Alamine-336 used as liquid extractant is a commercial product produced by General Mills Company. It is a mixture of long chain tertiary amines [M=363.3]. Tartaric acid (Merck Co.) as well as other reagents used here was of analytical grade purity.

Aqueous tartaric acid solution (% 10w) was prepared from distilled water. Organic phase is prepared by mixing solvents shown in Table 1 with Alamine-336 in 5 different concentrations. The extraction was performed by shaking equal volumes of initial aqueous and organic phases in a thermostated bath for 6 h. Thereafter the

Table 1. Physical Properties of Solvents

	Heptane	Toluene	Kerosene	MIBK	Isooctane
Density (g/cm^3), 20 °C	0,68	0.87	0.79	0.80	0.69
Viscosity (mPas), 20 °C	0.40	0.58	2	0.59	0.51
Boiling Point (°C)	98	111	150-300	116	99
Mole weight (g/g.mole)	100.21	92.14	-	100.16	114.23
Dielectric Const. *(e), 20 °C*	1.90	2.40	-	13.10	1.90
Firm	Merck	Carlo Erba	Tüpraş	Merck	Merck

Table 2: Experimental Results of The Extraction of Tartaric Acid with Alamine-336

Solvents	C_{A336} (mole/L)	$C_{TA,aq}$ (w. %)	$C_{TA,Org}$ (w. %)	D	Z
Heptane	0.38	7.99	3.38	0.42	0.161
	0.68	5.58	6.27	1.12	0.169
	1.28	2.40	9.78	4.07	0.150
	1.53	1.07	11.32	10.58	0.149
	1.75	0.61	11.68	19.14	0.137
Isooctane	0.36	9.47	1.17	0.12	0.059
	0.74	5.62	6.22	1.11	0.159
	1.07	3.55	8.86	2.50	0.162
	1.41	1.49	10.32	6.93	0.146
	1.83	0.51	10.71	21.00	0.121
MIBK	0.36	7.15	3.82	0.54	0.228
	0.74	3.50	8.00	2.29	0.239
	1.07	1.21	10.47	8.65	0..04
	1.41	0.59	11.05	18.72	0.163
	1.83	0.35	11.13	31.80	0.132
Kerosene	0.36	7.95	2.63	0.33	0.150
	0.72	5.38	5.63	1.05	0.161
	1.05	3.07	8.07	2.63	0.160
	1.41	1.40	10.05	7.18	0.149
	1.76	0.59	10.60	17.97	0.127
Toluene	0.37	7.36	3.15	0.43	0.187
	0.73	4.75	6.07	1.28	0,181
	1.39	0.96	9.93	10.34	0,161
	1.83	0.38	10.87	28.60	0.127
Kerosene + Toluene	0.35	7.60	2.90	0.38	0.175
	0.72	5.00	5.93	1.19	0.176
	1.07	2.67	8.46	3.17	0.168
	1.42	1.02	10.21	10.01	0.153
	1.77	0.44	11.20	25.45	0.130

mixture was kept 2-5 h to reach full separation of phases. Experiments were carried out at 25±0.1 °C. Acid concentrations were determined by volumetric titration with standardized NaOH.

Results and Discussion

Distribution coefficients and loading factors calculated from experimental results are presented in Table 2 and Fig. 1,2,3. As can be seen from Fig. 1 and 2, the distribution coefficient and loading factors increase with increasing Alamine-336 concentration for all diluents.

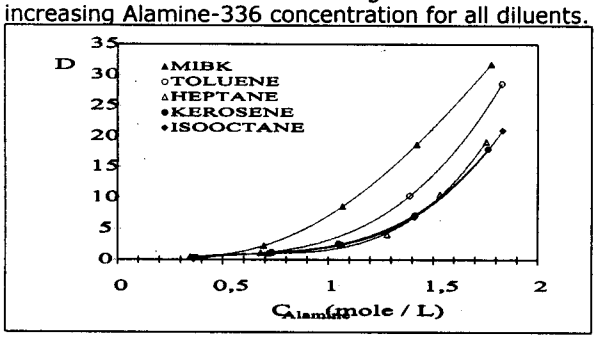


Fig. 1: Variation of Distribution Coefficients with Concentration of Alamine-336 in Different Diluting Solvents

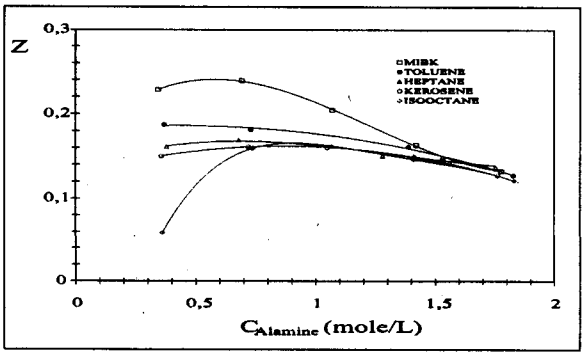


Fig. 2: Variation of Distribution Coefficients with Concentration of Alamine-336 in Different Diluting Solvents

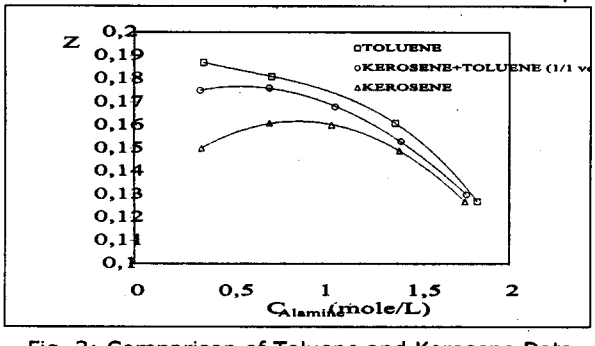


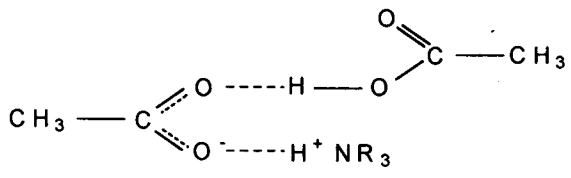
Fig. 3: Comparison of Toluene and Kerosene Data with Toluene-Kerosene Mixture

The extraction efficiency of the diluents can be presented as follows:

MIBK>Toluene>Heptane>Kerosene>Isooctane

This behavior can be expressed with formation of acid-amine complex. It can be shown as follows (Tamada and King 1990 (a) and (b)):

The interactions between the complex and diluent can be



divided into "general solvation" and "specific interactions" of the diluent with the complex. eptane and Isooctane being nonpolar, provide very little solvation of the polar complex. Toluene is an aromatic solvent and it produces slightly higher distribution coefficients, which has been rationalized as solvation due to interaction of the aromatic p electrons with complex. MIBK is polar and can promote extraction by providing a good solvating media for the ion pair.

Nomenclature

C_{336}	: Concentration of Alamine 336, (mole / L).
$C_{TA,org}$	: Concentration of tartaric acid in organic phase at the end of extraction, (W %).
$C_{tA,aq}$	: Concentration of tartaric acid in organic phase at the end of extraction, (W %) .
D	: Distribution Coefficient
Z	: Loading Factor
MIBK	: Methylisobutylketone
m_a	Total amount of acid in organic phase
m_e	Total amount of acid in organic phase

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