Partition Coefficients of Citric Acid between Aqueous Solutions and Long Chain Amines Dissolved in Various Solvents

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The extraction of citric acid from an aqueous solution into solutions of tri-n-octylamine and Alamine 336 in single solvents hexane, cyclohexane, toluene and methyl isobutyl ketone (MIBK) was investigated. Formation of acid amine complexes is a dominating factor in the system under consideration. Diluents were chosen from different chemical classes—polar and nonpolar—so as to examine the effect of diluents complex interactions. The partitation coefficients and loading factors were calculated and interpreted from experimental results.

Key Words: Extraction, Citric acid, Tri-n-octylamine, Alamine 336.

INTRODUCTION

Several authors[1-3] investigated the extraction of carboxylic acids by amines dissolved in organic solvents. It has been found that diluents, especially those with functional groups, can affect the extraction behaviour of amine significantly. The stoichiometry of solute : amine complex, loading of amine as well as the third phase formation are influenced by the diluent. The effect of diluent can be understood in terms of ability to solvate to organic phase species; therefore it is necèssary to distinguish between general solvation from electrostatic, dispersion or other forces and specific solvation due to hydrogen bonding[4].

The extraction process can be described by the reactions,

$$H_3A + R_3N = H_3A \cdot R_3N$$

$$H_3A + 2R_3N = H_3A \cdot (R_3N)_2$$
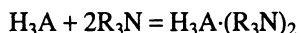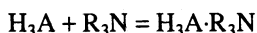
The resulting acid : amine complexes are supposed to be stabilized due to the hydrogen bonding with the diluent[5].

The structure of acid : amine complexes in diluents were determined by Barrow and Yerger[6]. They proposed that the first acid interacts directly with the amine to form an ion pair and the —OH of the carboxylic group of the second acid forms a hydrogen bonding with the conjugated —CO of the carboxylic group of the first acid to form a complex[7, 8].

In this work, experimental results for liquid-liquid equilibrium involved in the reactive extraction of citric acid with tri-n-octylamine and Alamine 336 dissolved

in single solvents hexane, cyclohexane, toluene and methyl isobutyl ketone (MIBK) at 25°C are presented.

Theoretical

An equilibrium description of acid-amine system can be written by a set of reactions of p-molecules of acid A and q-molecules of amine B to form various (p, q)-complexes with corresponding equilibrium constants, $K_{pq, true}$.

$$pA + q\overline{B} = \overline{A_pB_q} \tag{1}$$

$$K_{pq, true} = \frac{\overline{A_pB_q}}{[A]^p[\overline{B}]^q} \tag{2}$$

where species activities are denoted by brackets and the organic phase species are marked with an overbar. For practical application, the activities of the organic phase species are assumed to be proportional to the concentrations of the species, with the constants of proportionality taken up in the equilibrium constant. The apparent equilibrium constant for the overall reaction can be written as

$$B_{pq} = \frac{\overline{A_pB_q}}{[A]^p[B]^q} \tag{3}$$

where species concentrations are denoted by square brackets and are expressed in molar terms. The loading of the extractant Z is defined as the total concentration of acid in the organic phase, divided by the total concentration of amine in organic phase[9, 10]. With appropriate material balances Z is determined for a given set of stoichiometries as

$$Z = \frac{C_{A, org.}}{C_{B, tot}} = \frac{\Sigma\, pK_{pq}|A|^p|\overline{B}|^q}{C_{B, tot}} \tag{4}$$

Partitation coefficients for citric acid extracted from water into organic phase were determined as

$$D = \frac{[\text{Acid concentration in organic phase}]}{[\text{Acid concentration in aqueous phase}]} \tag{5}$$

EXPERIMENTAL

Tri-n-octylamine, citric acid and solvents were purchased from Merck Company. Alamine 336 a commercial product (Henkel Co.) was used; a mixture of straight-chain tertiary amines with seven to nine carbon atoms per chain containing 2.75 mol/kg of active amines (M = 363.3 g/mol). All chemicals were used without further purification.

Citric acid was dissolved in water to prepare the solutions with initial concentrations of acid 10% w/w. The initial organic phases were prepared by the dissolution of tri-n-octylamine and Alamine 336 in the diluents to produce solutions with approximately constant concentrations (1.80 mol/L, 1.40 mol/L, 1.10 mol/L, 0.40 mol/L).

For distribution experiments, equal volumes of an aqueous citric acid solution and an organic solution of amine were stirred in glass flasks in a temperature

controlled shaker bath at 25°C for 2 h, which preliminary tests demonstrated to be a sufficient time for equilibration. Thereafter, the mixture was kept in a bath for another 6–8 h to reach full separation of phases.

The concentration of the acid in the aqueous phase was determined by titration with aqueous sodium hydroxide (relative uncertainty: 1%)[11]. Acid analysis was checked against a material balance. In most cases the deviation between the amount of acid analyzed and the amount of acid known from preparing the solutions by weighing did not exceed 3%. The solubilities of amine salts and diluents in the aqueous phase were negligible in the range of variables investigated.

RESULTS AND DISCUSSION

Tables 1 and 2 present results of the experimental investigation. The concentrations of amines in solvents were between 0.40 mol/L 1.80 mol/L. The citric acid concentration in the initial aqueous phase was 10% by weight.

TABLE-1
EXTRACTION VALUES OF CITRIC ACID WITH TRI-*n*-OCTYLAMINE
IN DIFFERENT DILUTING SOLVENTS

Diluents	C_{TOA} (mol/L)	Z	D
Hexane	1.80	0.43	23.91
	1.40	0.48	8.90
	1.10	0.61	4.84
	0.70	0.49	0.98
	0.40	0.60	0.45
Cyclohexane	1.80	0.43	17.88
	1.40	0.52	1.41
	1.10	0.57	3.52
	0.70	0.58	7.70
	0.40	0.42	0.30
Toluene	1.80	0.44	32.44
	1.40	0.51	22.23
	1.10	0.69	11.69
	0.70	0.92	4.09
	0.40	0.53	0.37
MIBK	1.80	0.46	72.27
	1.40	0.57	60.00
	1.10	0.80	32.24
	0.70	1.09	12.00
	0.40	1.12	1.32

The equilibrium data on the distribution of citric acid between water and aliphatic amines (tri-n-octylamine and Alamine 336) dissolved in hexane, cyclohexane, toluene, methyl isobutyl ketone are presented in Table-1 and Table-2.

Fig. 1 demonstrates the influence of the organic solvent on citric acid distribution between water and tri-n-octylamine. It can be seen that the extraction power of tri-n-octylamine-diluent mixture changes with increasing initial concentration of tri-n-octylamine in the organic phase.

TABLE-2

EXTRACTION VALUES OF CITRIC ACID WITH ALAMINE 336 IN
DILUTING DIFFERENT SOLVENTS

Diluent	C_{A336} (mol/L)	Z	D
Hexane	1.80	0.43	15.31
	1.40	0.42	7.04
	1.10	0.65	3.08
	0.70	0.98	0.77
	0.40	0.45	0.30
Cyclohexane	1.80	0.42	11.54
	1.40	0.47	6.25
	1.10	0.46	1.75
	0.70	0.25	0.35
	0.40	0.45	0.32
Toluene	1.80	0.45	51.29
	1.40	0.52	27.84
	1.10	0.62	5.37
	0.70	1.13	1.69
	0.40	2.02	0.41
MIBK	1.80	0.46	60.85
	1.40	0.53	35.57
	1.10	0.68	10.61
	0.70	0.88	3.16
	0.40	0.90	0.85

According to Table-1 and Fig. 1 for tri-n-octylamine extraction, the following orders were found for the respective diluents:

MIBK > Toluene > Hexane > Cyclohexane

This fact can be explained by the formation of two or more acid : amine complexes, which are effected by the diluents in different ways.

Solvation of the complex by the diluent is a critical factor in the extraction of acid. The interactions between the complex and diluent can be divided into general solvation and specific interactions of the diluent with the complex. Inert diluents—hexane, cyclohexane—give a very low distribution of the acid into the solvent phase. Alkanes being nonpolar provide very low solvation of the polar complexes. Aromatic diluent (toluene) gives higher distribution, which has been rationalized as solvation due to interaction of the aromatic π electrons with

complex. MIBK is polar and can promote extraction by providing a good
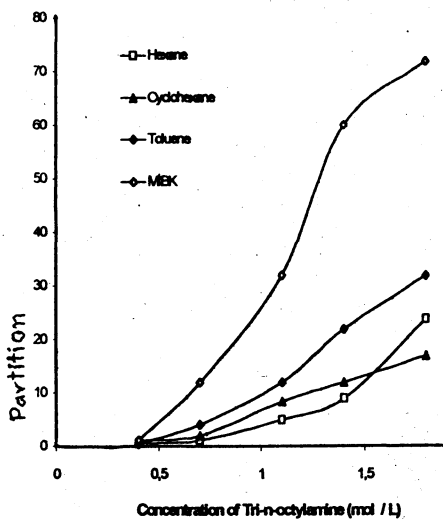solvating media for the ion pair.

Fig. 1. Variation of partitation coefficients with concentration of tri-n-octylamine in different
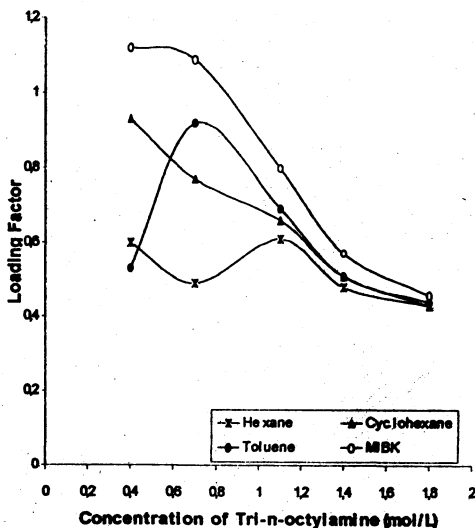diluting solvents.

Fig. 2. Variation of loading factors with concentration of tri-n-octylamine in different diluting
solvents.

In Fig. 2 the effect of tri-n-octylamine concentration on loading is shown. The
loading curve is a plot of Z *vs.* amine concentration. Overloading (loading greater
than unity) indicates that complexes with more than one acid per amine have been
formed. With MIBK overloading can be observed at low tri-n-octylamine
concentrations (Fig. 2).

Systems that include the diluent specifically in the complex stoichiometry show decreasing loading with increasing amine concentration. With all of the solvents at tri-n-octylamine extraction loading decreases, indicating that complexes include the diluent specifically (Fig. 2). Systems that exhibit aggregation, formation of complexes with large numbers of acid and amine molecules, exhibit an abrupt increase in loading. Toluene and hexane in tri-n-octylamine extraction (Fig. 2) exhibit abrupt increase at 0.4–1.4 mol/L amine concentration indicating that complexes include large numbers of acid and amine molecules.

For systems with only one amine per complex, there is no effect of total amine concentration on the loading. If there is more than one amine per complex loading increases with increasing amine concentration.

According to Table 2 and Fig. 3 for Alamine 336 extraction, the following orders were found for the respective diluents.
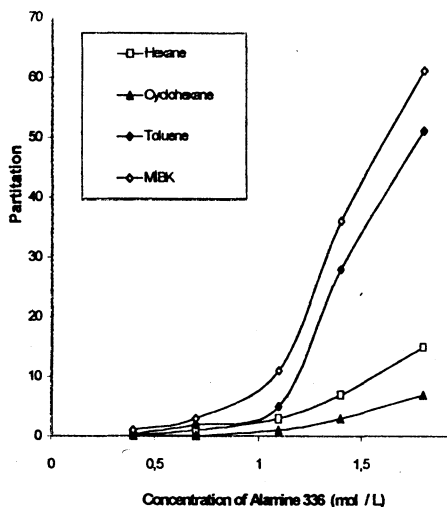
<div align="center">MIBK > Toluene > Hexane > Cyclohexane</div>

Fig. 3.   Variation of partitation coefficients with concentration of Alamine 336 in different diluting solvents.

Due to high polarity of MIBK and its capability to act as a hydrogen bond acceptor, citric acid shows a considerable solubility in that solvent in the presence of Alamine 336 (same as with tri-n-octylamine).

The effect of Alamine 336 concentration on loading is shown in Fig. 4. With toluene overloading can be observed at low concentration of Alamine 336. Hexane and cyclohexane exhibit abrupt increase at 0.6–1.5 mol/L amine concentration indicating that complexes include large numbers of acid and amine molecules. In cyclohexane, loading increases, indicating that complexes include more than one amine per complex and with other solvents loading decreases, indicating that complexes include the diluent specifically.
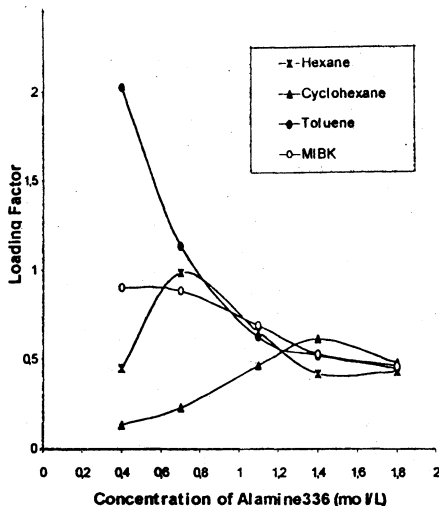
Fig. 4.   Variation of loading factors with concentration of Alamine 336 in different diluting solvents.

REFERENCES

Symbols

A = Acid

B = Amine

B_{pq} = Apparent equilibrium constant

C_{A336} = Concentration of Alamine 336 (mol/L)

C_{TOA} = Concentration of tri-n-octylamine (mol/L)

$C_{A, org}$ = Concentration of acid in organic phase at the end of extraction

$C_{B, tot}$ = Concentration of total amine in organic phase

D = Partitation coefficient

H_3A = Citric acid

$K_{pq, true}$ = Equilibrium constant

MIBK = Methyl isobutyl ketone

R_3N = Tertiary amine

p = Number of acid molecules

q = Number of amine molecules

Z = Loading factor

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