Distribution of Glycolic Acid Between Water and Different Organic Solutions

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The aim of this study is to present novel distribution data of glycolic acid between water and different organic solutions of trioctylamine and Alamine 336. Formation of acid amine complexes is a dominating factor in the system under consideration. Diluents are chosen from different chemical classes – polar and nonpolar – so as to examine the effect of diluents complex interactions. Diluting solvents used in this study are heptane, cyclohexane, toluene and methyl isobutyl ketone (MIBK). The distribution coefficients and loading factors are calculated and interpreted from experimental results.

Key words:
Extraction; glycolic acid; trioctylamine; alamine 336

Introduction

In the production of glycolic acid, processes produce multicomponent, aqueous solutions with product of acid concentrations typically w = 10 % at most and, usually, substantially less. Subsequent separation, purification and concentration of the acid recovery of carboxylic acids from fermentation broth, presents a challenging separations difficult because of high affinities of the acids for water distillation of dilute, non-volatile acid involves large energy consumption for the heat of vaporisation of water, which must be taken overhead, furthermore, distillation cannot fractionate among non – volatile acid.

The low aqueous activity of carboxylic acids results in low distribution coefficients of acid into conventional solvents. Thus, solvent extraction with conventional solvents would require very high solvent flow rates and result in substantial dilution of acid.

Aliphatic tertiary amines dissolved in an organic solvent are powerful extractants for carboxylic acids.[1–7] The amine binds the acid in the organic phase through reversible complexation. Often, water is taking part in complex formation, thus having a strong influence on the liquid-liquid equilibrium.[8–12]

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 necessary to distinguish between general solvation from electrostatic, dispersion or other forces, and specific solvation due to hydrogen bonding.[13]

The extraction process can be described by the reactions,

$$HORCOOH + 2NR_3 = HO–R–COO–H\text{---}NR_3$$

$$HORCOOH + 2NR_3 = HO–R–COOH–(NR_3)_2^-$$

The resulting acid:amine complexes are supposed to be stabilizied due to the hydrogen bonding with the diluent.[14–15]

The structure of acid-amine complexes in diluents were determined by *Barrow* and *Yerger* (1955). They proposed, that the first acid interacts directly with the amine to form an ion pair, and the OH of the carboxyl of the second acid forms a hydrogen bonding with the conjugated CO of the carboxylate of the first acid to form a complex (Figure 1).[16–17]

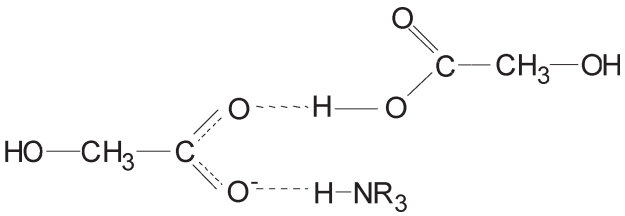

Fig. 1 – *The structure of acid – amine complex*

Several workers have investigated the extraction of different carboxylic acids by amines dissolved in organic solvents.[1–12] However, the data about the systems under consideration have not been found. In this work, experimental results for liquid-liquid equilibrium involved in the reactive extraction of glycolic acid with trioctylamine and Alamine 336, dissolved in single solvents heptane, 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 acid A, molecules and q amine B, molecules to form various (p,q) complexes with corresponding equilibrium constants, $K_{pq,true}$.

$$pA + qB = A_pB_{q,\ org} \quad (1)$$

$$K_{pq} = (a_{ApBq})_{org} \ / \ a_A{}^p \ a_B{}^q. \quad (2)$$

where the species activities are denoted by brackets. 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 the proportionality considered in the equilibrium constant. The apparent equilibrium constant for the overall reaction can be written as:

$$k_{pq} = c_{Ap,Bq,org} \ / \ c_A{}^p \ c_B{}^q{}_{,org}. \quad (3)$$

where species concentrations are denoted by square brackets and are expressed in molar terms. The loading of the extractant, R is defined as the total concentration of acid in the organic phase, divided by the total concentration of amine in organic phase.[18] With appropriate material balance R is determined for a given set of stoichiometries as :

$$R = (c_{A,org} / c_{B,tot}) = (p \ k_{pq}(c_A)^p \ (c_{B,org})^q) \ / \ c_{B,tot} . \quad (4)$$

Distribution coefficients (Nernstlow distribution) for glycolic acid, extracted from water into organic phase were determined as

$$D = c_{A,org} \ / \ c_A . \quad (5)$$

Experimental

Trioctylamine, glycolic acid and solvents were purchased from Merck Company. Alamine 336, a commercial product (Henkel Co.), was used as a mixture of straight-chain tertiary amines with seven to nine carbon atoms per chain containing 2.75 mole kg^{-1} of active amines (M = 363.3 g mole^{-1}). All chemicals were used without further purification.

Glycolic acid was dissolved in water to prepare the solutions with initial concentrations of acid w = 10 %. The initial organic phases were prepared by the dissolution of trioctylamine and Alamine 336 in the diluents to produce solutions with approximately constant concentrations (1.80 mole L^{-1}, 1.40 mole L^{-1}, 1.10 mole L^{-1}, 0.70 mole L^{-1}, 0.40 mole L^{-1}).

For distribution experiments, equal volumes of an aqueous glycolic acid solution and an organic solution of amine were stirred in glass flasks in a shaker bath at 25 °C for 2 h, what preliminary tests demonstrated to be a sufficient time for equilibration. Thereafter, the mixture was kept in a bath for another 6–8 h to complete separation of phases.

The concentration of the acid in the aqueous phase was determined by titration with aqueous sodium hydroxide (relative uncertainty: 1 %).[19] 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 by 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

Table 1 and 2 present results of the experimental investigation. The concentrations of amines in solvents were between 0.40 mole L^{-1} and 1.80 mole L^{-1}. The glycolic acid mass fraction in the initial aqueous phase was w = 10 % .

Table 1 – *Experimental results of the extraction of glycolic acid with trioctylamine in diluting solvents*

Diluent	c_{A336} mole L^{-1}	R	D
Heptane	1.80	0.57	2.17
	1.40	0.59	1.28
	1.10	0.51	0.66
	0.70	0.34	0.22
	0.40	0.19	0.06
Cyclohexane	1.80	0.61	2.92
	1.40	0.59	1.72
	1.10	0.60	0.84
	0.70	0.80	0.74
	0.40	0.76	0.31
Toluene	1.80	0.63	3.04
	1.40	0.71	1.97
	1.10	0.72	1.20
	0.70	0.71	0.54
	0.40	0.17	0.05
MIBK	1.80	1.02	4.04
	1.40	0.87	3.93
	1.10	0.86	1.73
	0.70	0.92	0.70
	0.40	0.50	0.60

Table 2 – *Experimental results of the extraction of glycolic acid with Alamine 336 in diluting solvents*

Diluent	c_{A336} mole L^{-1}	*R*	*D*
Heptane	1.80	0.58	2.26
	1.40	0.59	1.28
	1.10	0.48	0.60
	0.70	0.41	0.26
	0.40	0.29	0.09
Cyclohexane	1.80	0.56	2.19
	1.40	0.61	1.44
	1.10	0.49	0.64
	0.70	0.38	0.24
	0.40	0.11	0.03
Toluene	1,80	0.64	3.09
	1,40	0,71	1.97
	1,10	0,72	1.20
	0,70	0,67	0.50
	0,40	0,20	0.06
MIBK	1.80	0.69	4.21
	1.40	0.73	2.16
	1.10	0.76	1.33
	0.70	1.12	1.15
	0.40	1.10	0.40

The equilibrium data on the distribution of glycolic acid between water and aliphatic amines (trioctylamine and Alamine 336) dissolved in heptane, hexane, cyclohexane, isooctane, toluene, methyl isobutyl ketone, are presented in Table 1 and Table 2.

Figure 2 demonstrates the influence of the organic solvent on glycolic acid distribution between water and trioctylamine. It can be seen that the extraction power of trioctylamine – diluent mixture changes with increasing initial concentration of trioctylamine in the organic phase.

According to Table 1 and Figure 2 for trioctylamine extraction the order was as follows:

MIBK > Toluene > Cyclohexane > Heptane.

This fact can be explained by the formation of two or more acids: 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 – heptane, 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) give 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.

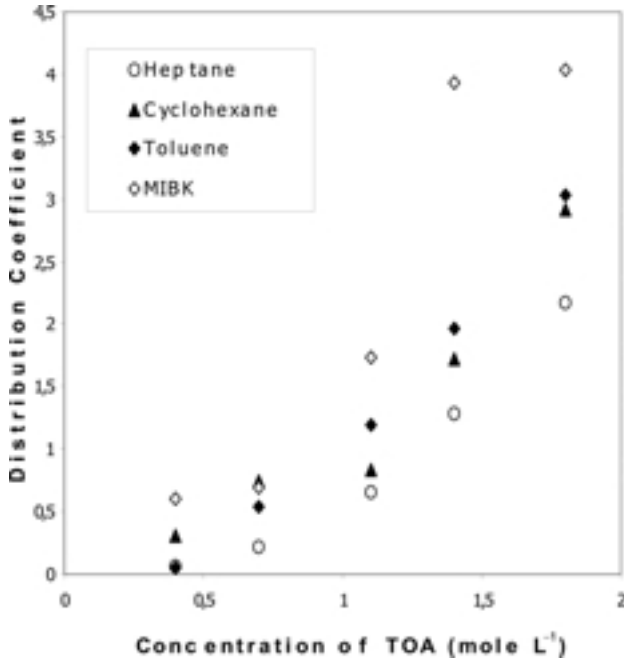

Fig. 2 – *Variation of distribution coefficients with concentration of Trioctylamine in different diluting solvents.*

In Figure 3 the effect of trioctylamine concentration on loading is shown. The loading curve is a plot of *R* 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 high trioctylamine concentrations (Figure 3).

Systems that include the diluent, specifically in the complex stoichiometry, show loading decrease with increase of amine concentration. With cyclohexane at trioctylamine, extraction loading decreases, thereby, indicating that complexes include the diluent specifically (Figure 3). Systems that exhibit aggregation, formation of complexes with large numbers of acid and amine molecules, exhibit an abrupt increase in loading. Toluene, MIBK, and heptane at trioctylamine extraction (Figure 3) exhibit abrupt increase at low amine concentrations, thereby, indicating that complexes include large number of acid and amine molecules.

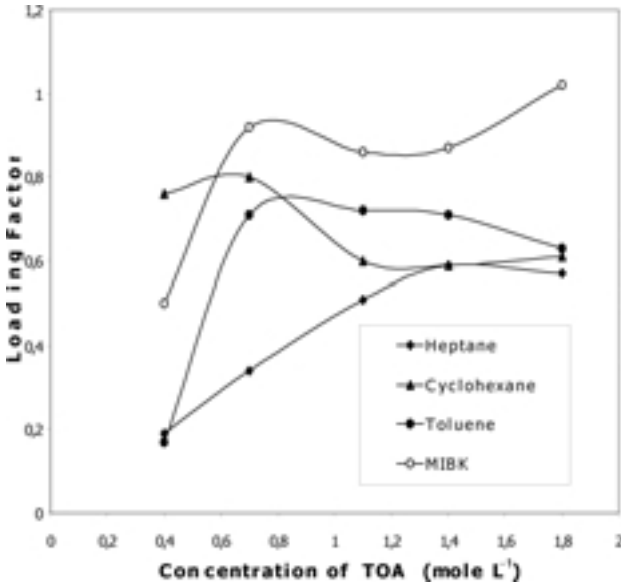

Fig. 3 – *Variation of loading factors with concentration of Trioctylamine in different diluting solvents*

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 Figure 4, for Alamine 336 extraction the following orders were found:

MIBK > Toluene > Heptane > Cyclohexane.

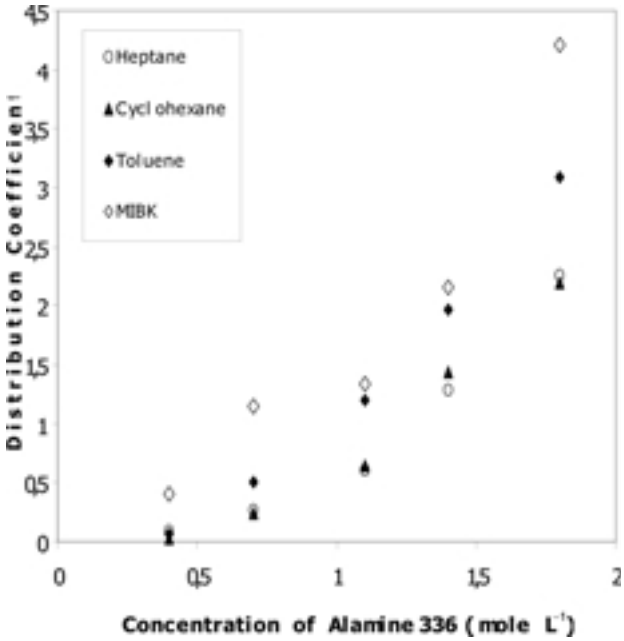

Fig. 4 – *Variation of distribution coefficients with concentration of Alamine 336 in different diluting solvents*

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

In Figure 5, the effect of Alamine 336 concentration on loading is shown. With MIBK overloading can be observed at low Alamine 336 concentrations. Toluene exhibit abrupt increase, thereby indicating that complexes include large number of acid and amine molecules. With MIBK loading increases, thereby indicating that complexes include more than one amine per complex and with other solvents loading decreases, thereby indicating that complexes include the diluent specifically.

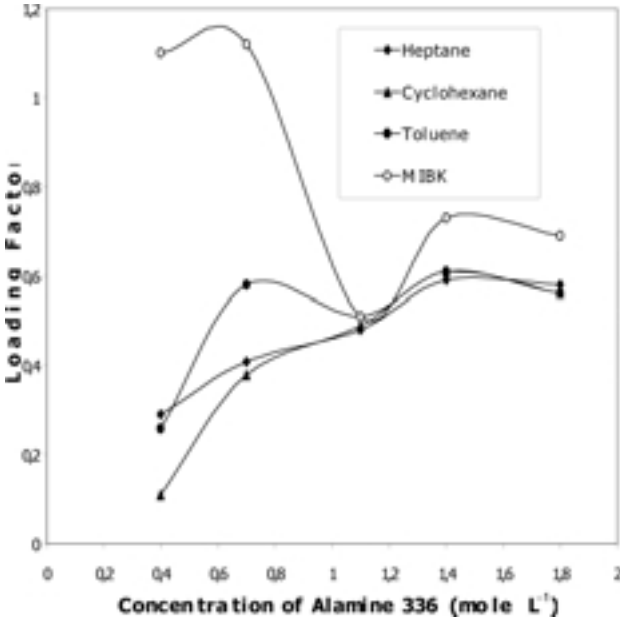

Fig. 5 – *Variation of loading factors with concentration of Alamine 336 in different diluting solvents*

Symbols

$A_pB_{q,org}$ – Complex in organic phase
$a_{ApBq,org}$ – Activity of complex in organic phase
a_A – Activity of acid
a_B – Activity of amine
k_{pq} – Apparent equilibrium constant
c_{A336} – Concentration of Alamine 336, mole L^{-1}
c_A – Concentration of acid in aqueous phase, mole L^{-1}
$c_{ApBq,org}$ – Concentration of complex in organic phase, mole L^{-1}
$c_{A,org}$ – Concentration of acid in organic phase, mole L^{-1}
c_{TOA} – Concentration of trioctylamine, mole L^{-1}
$c_{B,tot}$ – Concentration of total amine in organic phase, mole L^{-1}
D – Distribution coefficient
HORCOOH – Glycolic acid

$K_{pq,\text{true}}$ – Equilibrium constant
p – Number of acid molecules
q – Number of amine molecules
R_3N – Tertiary amine
R – Amount ratio
w – mass fraction, %

Abbreviations

A – Acid
B – Amine
MIBK – Methyl isobutyl ketone

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