

Reactive Extraction of Citric Acid Using Different Extractants: Equilibrium, Kinetics and Modeling



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Recovery of citric acid from biotechnologically produced low concentration aqueous solution has attracted several separation techniques for the downstream processing. Amongst them, reactive extraction is a convenient, cheap, and effective method. Three different extractants are used in this study, namely tri-*n*-butyl phosphate (TBP), tri-*n*-octylamine (TOA), and Aliquat 336 (A336), all diluted in methyl-iso-butyl ketone (MIBK). The isothermal batch experiments were performed for the equilibrium and kinetic studies at $T = 300.15 \pm 1$ K. Around 92 % extraction efficiency (E %) was obtained using 20 % (v/v) TOA in MIBK. Based on the overloading of amine ($Z > 0.5$), (2:1) acid:extractant complex in TOA+MIBK phase was proposed. Kinetics of extraction of citric acid (0.2 – 0.8 kmol m^{-3}) was also performed in a Lewis-type stirred cell, using TOA in MIBK. The extraction reaction was occurring in the diffusion film. The second order rate constant was calculated as $k_2 = 0.0351$ m^3 kmol $^{-1}$ s $^{-1}$. The extraction parameters were estimated by differential evolution optimization technique. Optimal value of equilibrium constant, K_E , was found to be $3.6 \cdot 10^{-3}$ (m^3 kmol $^{-1}$)², for the reactive extraction of citric acid using 20 % TOA in MIBK, and was found in close agreement with experimental values.

Keywords:

reactive extraction, citric acid, differential evolution, modeling, equilibrium, kinetics

Introduction

In a recent study, the demand for citric acid is reported to be increasing at a rapid rate of 5 % per year with predictions of its value in the global market at USD 3.6 billion toward 2020 in both liquid and anhydrous form.¹ This compound bearing the chemical formula $C_6H_8O_7$ (2-hydroxypropane-1,2,3-tricarboxylic acid), has phenomenal physicochemical properties: high solubility in water, palatability, chelating power and nontoxicity, etc. It is most common among carboxylic acids and naturally occurs in citrus fruits. The applications in food and beverages industries as acidulate, as well as in other pharmaceutical and chemical products have put the acid in the category of valuable products. It is used as an additive to many drinks to enhance flavor, to increase stability in soft drinks and syrups, and it is also used to prevent color change by oxidation.² It is used in citrus juices to improve taste and increase shelf life.³ The production of citric acid through bio-route is emerging as a promising alternative for the synthetic route due to ever-increasing prices of petroleum feedstocks.⁴ The downstream processing, i.e. separation of acid from aqueous solution is a

challenging task, and costs almost half the production cost. Therefore, an efficient alternative separation technology is required to make the overall recovery process economically feasible. At present, the commonly used recovery methods employed are electro dialysis, membrane separation, precipitation, crystallization, and so forth. However, each method has its own limitations and drawbacks. Recently, reactive extraction has emerged as more economic and convenient over other recovery techniques.^{5–7} It is especially suited when the product to be recovered is inhibitory and concentration is less than 10 wt %.^{5,6} It matches the conditions in a fermentation broth and thus this promising technology has been widely adopted for carboxylic acid recovery.

The extraction combined with chemical reaction offers efficient separation. The reactive species used for this purpose are extractants that very specifically extract carboxylic acids leaving behind foreign compounds in the fermentation broth. The first category of extractants include carbon-bonded oxygen donor that consists aliphatic, aromatic, and substituted hydrocarbon solvents. Secondly, there are phosphorus-bonded oxygen donor extractants, such as tri-*n*-butyl phosphate (TBP), trioctyl phosphine oxide (TOPO), etc., and third category com-

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prises of high molecular weight aliphatic amine extractants, such as tri-*n*-octyl amine (TOA), Aliquat 336 (A336), etc.^{5–9} As these extractants are costly as well as viscous, they are often employed after dilution in some conventional solvent (diluent). The diluent provides the desired solvation media to the extractant by tuning its desired physicochemical properties. Diluents are classified into inactive and active diluents, where the former includes aliphatic and aromatic hydrocarbons, and the latter has a functional group attached to it, such as alcohols, ketones, esters, ethers, etc. Doubtlessly, active diluents provide a better solvation media to the carboxylic acid, and hence show greater efficiency.⁵

Although studies on reactive extraction of various carboxylic acid are abundant in literature, the same for complete extraction study (equilibrium, kinetics and modeling) for citric acid are limited, a handful of research work can be found in the literature including equilibrium^{5–12} and kinetic studies^{12–13} of citric acid extraction. Bizek *et al.*⁹ were the first to study the physical and reactive extraction equilibria of citric acid in different diluent and trialkylamine as an extractant. The tertiary amine (e.g. TOA) reacts with the undissociated form of acid to give salts.⁸ The affinity to citric acid solvation of active diluents having different functional group are observed in the order of chloroform < aromatics < MIBK < octanol. They reported the acid-amine, acid-(amine)₂ complexes for extraction of citric acid that confirm the overloading of acid by trialkylamine. Aiming for a higher degree of extraction, Nikhade *et al.*¹⁰ used 30 % Alamine 366 in methylisobutylketone (MIBK) and found the distribution coefficient up to 67.147. They proposed the extraction accompanied by chemical reaction with a second order rate constant 0.013 m³ kmol⁻¹ s⁻¹. Poposka *et al.*¹² studied the extraction equilibria and kinetics using isodecanol/*n*-paraffin solution of TOA. They reported the value of Z_{\max} lying between 0.67–0.54 and suggested the existence of various stoichiometry.

The experimental and modeling studies on reactive extraction equilibria of citric acid using TBP, TOA, and A336 as extractants diluted in butyl acetate, decanol, and benzene has been published in our previous article.¹⁴ Among the active diluents, MIBK has been reported in the literature as an efficient solvent for physical extraction of citric and other carboxylic acids.¹⁵ Nevertheless, it provides a good solvation medium to the extractants such as TOA, Alamine 336, etc. However, the experimental data is lacking in the literature for comparative studies on equilibrium behavior of different extractants and MIBK as a diluent. The present work aims at analyzing the extraction efficiency and liquid-liquid equilibria of citric acid using TBP, TOA, and A336 in MIBK. The stoichiometry of acid-extract-

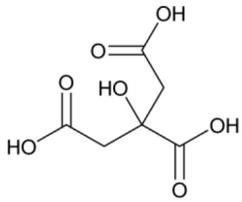
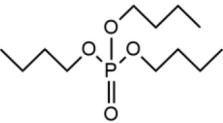
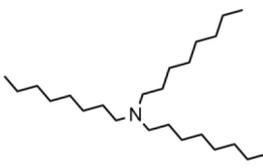
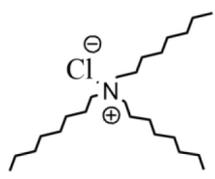
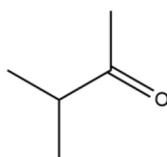
ant complex in these three systems was analyzed graphically, as well as using the modeling approach with differential evolution¹⁶ as an optimization technique. This apart, investigating TOA+MIBK system as the most efficient extraction system in the extraction equilibrium studies, the same has been chosen for the kinetic studies of reactive extraction of citric acid from dilute aqueous solutions.

Experimental

Materials

Citric acid was obtained from Merck Co. Ltd. India. The extractants, tri-*n*-octylamine (TOA) and A336 were supplied by Sigma Aldrich, India; and tri-*n*-butyl phosphate (TBP) was received from Loba Chemie, India. The Millipore (Merck) purified water was used for preparing the aqueous solutions. All the chemicals used were of analytical grade and used as received. The physicochemical properties of reagents used in the present study are summarized in Table 1.

Table 1 – Physicochemical properties of chemicals used

Chemical name	Molecular formula	Structure	Purity/%
Citric acid	C ₆ H ₈ O ₇		98
TBP	C ₁₂ H ₂₇ PO ₄		98
TOA	C ₂₄ H ₅₁ N		99
A336	C ₂₅ H ₅₄ NCl		98
MIBK	C ₃ H ₇ (C)OCH ₃		99

Methods

Equilibrium studies

Through the bio-route, citric acid was produced in $\sim 0.53 \text{ kmol m}^{-3}$ concentration, and hence, the low concentration of aqueous phase ($0.2\text{--}0.8 \text{ kmol m}^{-3}$) was prepared and used.¹⁷ The different percentage of extractant (10–50 % (v/v)) dissolved in diluents, MIBK, were taken for the equilibrium studies. An equal amount of organic phase (extractant+MIBK) and aqueous phase (citric acid solution) were taken and mixed for 2 hours in a temperature-controlled water bath shaker (Remi Equipment Pvt. Ltd., India) at $T = 300.15 \pm 1 \text{ K}$. The samples were allowed to settle for clear phase separation for 4 h. Shaking time and settling time was optimized in separate experiments. Citric acid concentration in the aqueous phase was determined by HPLC system (Young Lin Instruments, South Korea) equipped with a quaternary pump and vacuum degasser. A reverse phase column C-18, and a UV/Vis detector at 210 nm were used. Mobile phase was an aqueous solution of phosphoric acid and potassium di-hydrogen phosphate, with a flow rate of 0.6 mL min^{-1} .¹⁷ Samples were sonicated and filtered through a Ran Disc $0.22 \mu\text{m}$ PTFE membrane before injection into HPLC. To ensure the reproducibility of results, all analyses were repeated twice under identical conditions, and consistency was within $\pm 2 \%$. The mean value was used for further calculations. Acid concentration in organic phase was obtained by material balance.

Kinetic studies

Kinetics experiments for citric acid extraction were performed in a Lewis-type stirred cell that was designed similar to that used by Wasewar *et al.*¹⁸ and Gaidhani *et al.*¹⁹ The cell was configured with a flat bottom with 6.5 cm inner diameter, and having total interfacial area of 33.18 cm^2 . The stirred cell was firstly filled with 100 mL aqueous solution of citric acid of different concentrations. The dual stirrer with four-flat blade paddle of 4.8 cm in diameter and 1 cm in width, was adjusted to 1 cm below and above the interface of aqueous and organic phase. A known volume (100 mL) of the organic mixture of extractant (TOA) and diluent (MIBK) were then added in the vessel, and reactive extraction was carried out for a definite period. The sampling volume was kept low (1 mL), so that volume change is negligible.

Theory

Reactive extraction equilibria

The reactive extraction equilibrium of tricarboxylic acid using different extractants (E) can be

represented by Eq. 1, which shows the acid:extractant complex formation at the interphase⁷.



where, m and n are the stoichiometric coefficients, and the bar over the species represents the organic phase. The extraction equilibrium constant could be defined as Eq. 2.

$$K_E = \frac{\overline{[(\text{H}_3\text{A})_m E_n]}}{[\text{H}_3\text{A}]^m [\bar{E}]^n} = \frac{\overline{[(\text{H}_3\text{A})_m E_n]} (1 + K_a / [\text{H}^+])^m}{[\text{H}_3\text{A}]_T^m [\bar{E}]^n} \quad (2)$$

where, $[\text{H}_3\text{A}]_T$ is the total (ionized+unionized) acid concentration and K_a is the dissociation constant of citric acid. Also, distribution coefficient of the acid between aqueous and organic phase may be correlated as Eq. 3.

$$K_D = \frac{\overline{[\text{H}_3\text{A}]}}{[\text{H}_3\text{A}]_T} = m \frac{\overline{[(\text{H}_3\text{A})_m E_n]}}{[\text{H}_3\text{A}]_T} \quad (3)$$

The Eq. 2 and Eq. 3 may be combined to derive the relation between equilibrium constant and distribution coefficient as represented by Eq. 4.

$$K_E = \frac{K_D (1 + K_a / [\text{H}^+])^m}{m [\text{H}_3\text{A}]_T^{m-1} [\bar{E}]^n} \quad (4)$$

The extractant concentration at equilibrium $[\bar{E}]$ can be obtained by using Eq. 5.

$$[\bar{E}] = [\bar{E}]_{\text{in}} - K_D n [\text{H}_3\text{A}]_T / m \quad (5)$$

By combining Eqs. 4 and 5, a model equation is developed, which can be used to obtain optimized values of K_E , m , and n using numerical approach¹⁵.

$$K_D = m K_E \left([\bar{E}]_{\text{in}} - K_D n \frac{[\text{H}_3\text{A}]_T}{m} \right)^n \frac{[\text{H}_3\text{A}]_T^{m-1}}{(1 + K_a / [\text{H}^+])^m} \quad (6)$$

The acid-extractant complex formation can also be predicted using loading ratio (Z). It is defined as the extent to which the organic phase (extractant + diluent) can be loaded with acid:

$$Z = \frac{\overline{[\text{H}_3\text{A}]}}{[\bar{E}]} \quad (7)$$

The value of Z depends upon the extractability of the acid, its aqueous concentration, and the nature of the extractant. Thus, for lower loading of amine i.e. $Z < 0.5$, (1:1) acid: TOA complex formation can be assumed and K_E is related to Z as:²

$$\frac{Z}{1-Z} = K_{E1} [\text{H}_3\text{A}] \quad (8)$$

where, K_{E1} is equilibrium complexation constant for (1:1) acid:TOA complex. However, in the case of higher loading values, that is ($Z > 0.5$), complexes with higher stoichiometry are also formed. For (2:1) acid:TOA complex formation, the corresponding relation can be written as,

$$\frac{Z}{2-Z} = K_{E2} [H_3A]^2 \quad (9)$$

where, K_{E2} is equilibrium complexation constant for (2:1) acid:TOA complex. Eq. 9 and Eq. 10 can be used for determining the equilibrium complexation constant and stoichiometry of acid-extractant complex graphically by fitting the experimental data.

The modified loading ratio (Z_m) is introduced to evaluate the loading by extractant only that can be obtained by subtracting contribution by diluents alone from the total loading values, Z , as:

$$Z_m = Z - \nu\mu; \text{ where, } \mu = \frac{[H_3A]^{\text{diluent}}}{[E]^0} \quad (10)$$

Consequently, Eq. (8) and Eq. (9) could be modified to Eq. (11) and Eq. (12), respectively.

$$\frac{Z_m}{1-Z_m} = K_{E1} [H_3A] \quad (11)$$

$$\frac{Z_m}{2-Z_m} = K_{E2} [H_3A]^2 \quad (12)$$

Reactive extraction kinetics

Doraiswamy and Sharma²⁰ proposed the kinetic theory of extraction accompanied with chemical reaction to determine its effect on the specific rate of mass transfer. Differential mass balance of the batch system for the organic phase can be presented as Eq. 13:

$$\frac{d[H_3A]}{dt} = k_L \left(\frac{A_c}{V_{\text{org}}} \right) \left(\overline{H_3A}^* - \overline{H_3A} \right) \quad (13)$$

where, k_L represents physical mass transfer coefficient whereas, $\overline{H_3A}^*$ and $\overline{H_3A}$ are equilibrium and aqueous phase acid concentrations, respectively. They used the film and renewal theories with physicochemical and hydrodynamic parameters, and classified the systems into four regimes depending on their relative diffusion and reaction rates.

Regime 1: Very slow reaction occurring in the bulk liquid phase with practically no reaction in the liquid film. Regime 2: Slow reaction in which the diffusion rate is higher than the rate of the homogeneous bulk phase reaction. Regime 3: Fast reaction occurring in the diffusion film. Regime 4: Instantaneous reaction in which the reaction is so fast that

the two reactants cannot co-exist and a reaction plane is formed in the diffusion film.

The discerning mechanism is suggested by Doraiswamy and Sharma²⁰ for the extraction accompanied with a chemical reaction in a stirred cell. The expression for Regime 1, extraction accompanied by a slow general order chemical reaction is:

$$R_A \propto l [H_3A]^m [E^0]^n \quad (14)$$

Thus, Eq. 14 can be written as:

$$R_A = lk_{mn} [H_3A]^m [E^0]^n \quad (15)$$

where, R_A is the specific rate of extraction, l is the liquid volume hold-up of extractant (E) phase based on the total liquid volume, and k_{mn} is the specific rate constant. In the present study, R_A was obtained by varying the initial concentration of citric acid in the organic phase. Only initial rates were taken into consideration to avoid problems due to reversibility of extraction reaction. The condition for the reaction to fall into Regime 1 is given as:

$$k_L [H_3A] \gg lk_{mn} [H_3A]^m [E^0]^n \quad (16)$$

Parameter determination using differential evolution technique

The stoichiometry of the acid:extractant complex should be known for design of extractor. This can be predicted using the Chemodel given by Eq. (6).¹⁸ There are two parameters to be determined, i.e. K_E and m by setting n equal to unity. The optimization technique adopted in this study is the differential evolution, which is based on the genetic algorithm. This method is useful as it finds the global optimum, while the gradient-based techniques may trap into the local optimum. The objective function based on least squares error between experimental and model values of K_D were minimized for predicting the acid amine (TOA) stoichiometry, m and n for the complexation reaction.

$$\text{Objective function} = \sum_{\text{data points}} (k_D^{\text{exp}} - k_D^{\text{mod}})^2 \quad (17)$$

Results and discussion

The equilibrium studies were carried out for three systems, namely TOA, TBP and A336 diluted in MIBK. Being the best extraction system, TOA+MIBK was chosen for the kinetics studies. Finally, the loading of amine was predicted using the differential evolution algorithm.

Equilibrium distribution of citric acid

The equilibrium distribution of citric acid is shown in Fig. 1, for both physical (using MIBK

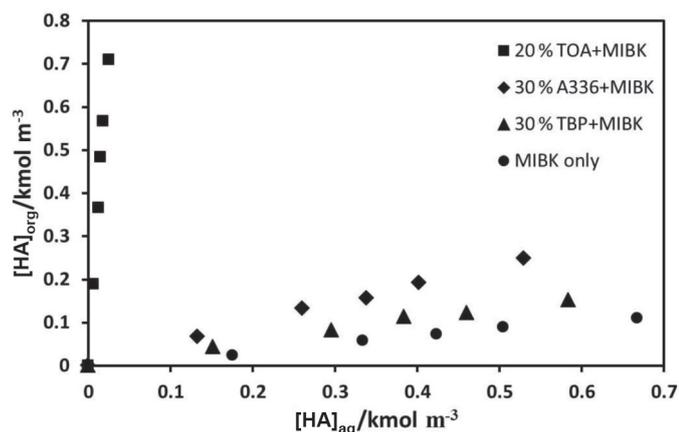


Fig. 1 – Equilibrium distribution isotherms for reactive extraction of citric acid ($0.2\text{--}0.8\text{ kmol m}^{-3}$) using different extractants at $T = 300 \pm 1\text{ K}$

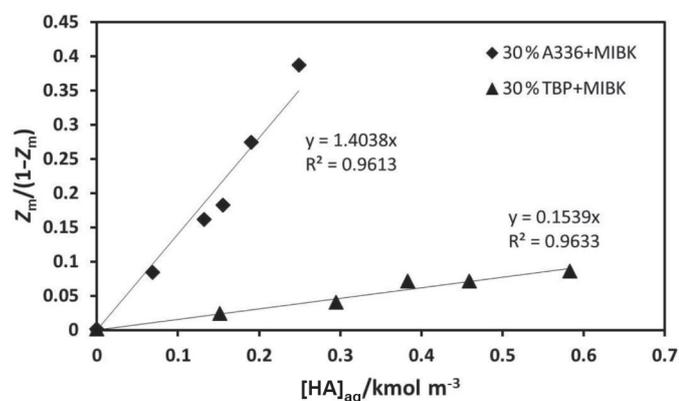


Fig. 2 – Estimation of equilibrium constant for reactive extraction of citric acid using 30 % (v/v) TBP+MIBK and 30 % (v/v) Aliquat 336 +MIBK extraction systems

only) and chemical [extractant (TOA/TBP/A336) + MIBK] extraction. Note that the extractants TBP and A336 in a concentration above 30 % (v/v) significantly extract the acid, while TOA is more efficient, even its 20 % concentration is able to extract more than 90 % of acid from aqueous phase. This is why the concentration of TOA is kept 20 % (v/v) and the same for TBP and A336 is 30 % (v/v).

MIBK alone is not able to provide significant extraction ($E \sim 14.93\%$). Both the partitioning coefficient (P) and dimerization constant (D) of MIBK were found to be around 0.152 and 0.795 that resulted in a low distribution coefficient ($K_D = 0.175$). For chemical extraction of citric acid, MIBK as a diluent unusually provides high distribution coefficients, even higher than what would be expected from polarity arguments alone. Thus, extraction efficiency was improved significantly when 30 % (v/v) TBP ($E = 20\text{--}22\%$) in MIBK was used. The use of extractant 30 % (v/v) A336 in MIBK could improve extraction up to 34.16 %. However, when 20 % (v/v) concentration of TOA in MIBK was

used remarkable extraction efficiency as high as 92.75 % was achieved, while Nikhade *et al.*¹⁰ had reported distribution coefficient of 67.147 ($E = 98.5\%$) using Alamine 336 diluted in MIBK. The extraction efficiency calculated in this work is in good agreement with the literature.^{10,12}

The stoichiometry of acid:extractant complex was estimated for chemical extraction of citric acid for all three extraction systems (A336, TBP, and TOA; diluted in MIBK). For TBP and A336, loading ratios (Z) were obtained to be low ($Z < 0.5$), thus, only (1:1) acid:extractant complex formation was assumed. The equilibrium complexation constant (K_{E1}) was estimated by graphical interpretation. Since MIBK is an active diluent (presence of --C=O group), its contribution in extraction cannot be neglected. Hence, the net extraction by the extractants can be calculated using the modified loading ratio (Z_m), which is obtained after subtracting the loading by the diluents alone from the overall loading. The plot of $Z_m/(1-Z_m)$ vs $[\text{HA}]_{\text{aq}}$ for A336 and TBP is presented in Fig. 2. The equilibrium complexation constant (K_{E1}) was obtained by regression analysis through linear fitting of equilibrium distribution data. The slope of these loading curves (Eq. 12) directly gives the K_{E1} values that were estimated to be $1.405\text{ m}^3\text{ kmol}^{-1}$ and $0.154\text{ m}^3\text{ kmol}^{-1}$ for 30 % (v/v) A336+MIBK and 30 % (v/v) TBP+MIBK, respectively.

In extraction involving TOA, there is a marked effect of the presence of TOA on the extraction of acid (Fig. 1). Higher loading ratios ($Z > 0.5$) were obtained in the studied concentration range of acid and amine, when TOA in MIBK was used as extractant. Kertes and King⁸ suggested that, for Z values greater than 0.5 (overloading of amine), higher stoichiometry complexes are possible.

Using Fig. 3, equilibrium complexation constant (K_{E2}) for (2:1) complex was estimated for the extraction of citric acid using TOA in MIBK. According to Eq. 12, from the plot of $Z_m/(2-Z_m)$ vs $[\text{HA}]_{\text{aq}}$, the value of K_{E2} was obtained as $3715.1\text{ (m}^3\text{ kmol}^{-1})^2$. The higher K_E value obtained using MIBK reveals its capacity to provide better solvation media, and hence, enhanced stability for acid:amine complex.

Kinetics of extraction of citric acid

Kinetics of extraction of citric acid ($0.2\text{--}0.8\text{ kmol m}^{-3}$) have been investigated using extractant TOA diluted in MIBK. The variation of organic phase citric acid concentration with time is shown in Fig. 4. Using 5 % TOA in MIBK, the specific rates of extraction were found to be 0.106, 0.087, and $0.065\text{ kmol m}^{-3}\text{ min}^{-1}$, when initial concentrations of citric acid were kept at 0.8 kmol m^{-3} , 0.6

kmol m^{-3} , and 0.4 kmol m^{-3} , respectively (Fig. 4). When there was no change in aqueous phase acid concentration, i.e. the time versus concentration curve became horizontal to time axis, the extraction time was optimized accordingly (60 min).

Physical mass transfer coefficient

For the transfer of citric acid from the aqueous phase to MIBK, the physical mass transfer coefficient (k_L) was measured to be $0.000549 \text{ kmol (s m}^2)^{-1}(\text{kmol m}^{-3})^{-1}$ at a speed of agitation (N) of 1.3 rev s^{-1} (Fig. 5). Further, to verify the regime of extraction reaction, kinetic experiments were performed. k_L was measured as a function of speed of agitation by contacting the aqueous solution of citric with the diluents, MIBK alone, at different speeds of agitation. Differential mass balance of the batch system for the organic phase can be presented as Eq. 18.

$$\frac{d[\overline{\text{HA}}]}{dt} = k_L \left(\frac{A_c}{V_{\text{org}}} \right) (\overline{\text{HA}}^* - \overline{\text{HA}}) \quad (18)$$

where, $\overline{\text{HA}}^*$ represents the organic phase acid concentration at equilibrium state. A correlation between k_L and N is established as given in Eq. 19.

$$k_L = 0.000567 N^2 \quad (19)$$

Reaction regimes

Experiments were conducted to observe the effects of the volume ratio of the phases and the speed of agitation on the specific rate of extraction using $0.114 \text{ kmol m}^{-3}$ TOA in MIBK at 0.4 kmol m^{-3} aqueous solution of citric acid.

Effect of agitation speed

To find the effect of the agitation speed, kinetic experiments were carried out by keeping the initial acid concentration (0.4 kmol m^{-3}) and the volume ratio (1:1) of the phases constant. In order to have an interfacial area equal to that of the geometric area during extraction, the interface was maintained flat by keeping low speed of stirring ($1.30\text{--}2.10 \text{ rev s}^{-1}$). It is known that, at low agitation rates, the surface is not completely renewed during stirring. Thus, under these conditions, the transfer of the acid is controlled by mass transfer resistances. At higher mixing rates, the interface was disturbed and had an interfacial area greater than the geometric area. Fig. 6 shows that the specific rate of extraction does not vary significantly with speed of agitation. For the subsequent experiments, the speed of agitation was kept constant at 1.30 rev s^{-1} .

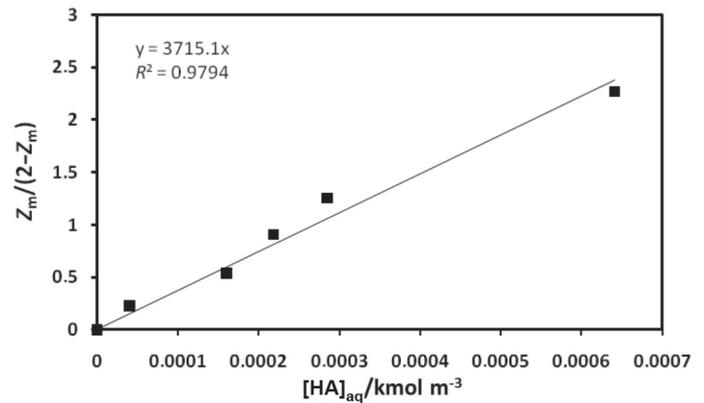


Fig. 3 – Estimation of equilibrium constant for reactive extraction of citric acid using 20 % (v/v) TOA + MIBK extraction system

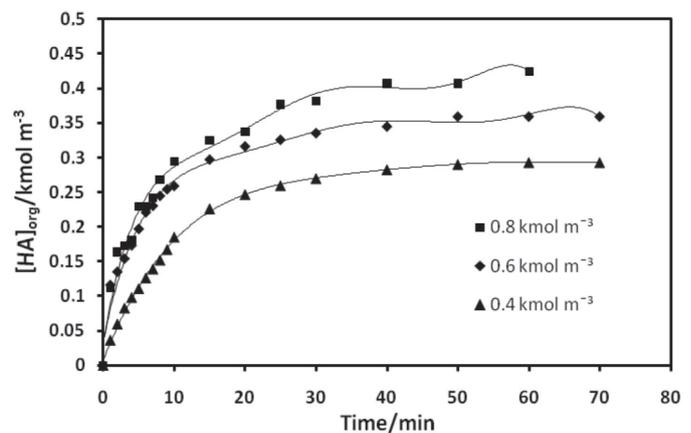


Fig. 4 – Variation of organic phase citric acid concentration with extraction time

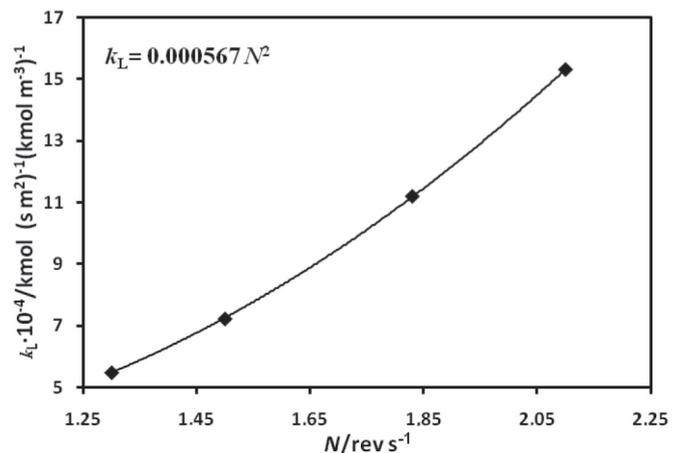


Fig. 5 – Effect of speed of agitation on physical mass transfer coefficient for reactive extraction of citric acid (0.8 kmol m^{-3}) with 5 % TOA in MIBK

Effect of volume phase ratio

In order to evaluate the effect of the volume ratio of the phases on the specific rate of extraction, experiments were conducted by keeping constant the concentration of the phases (0.8 kmol m^{-3}) and

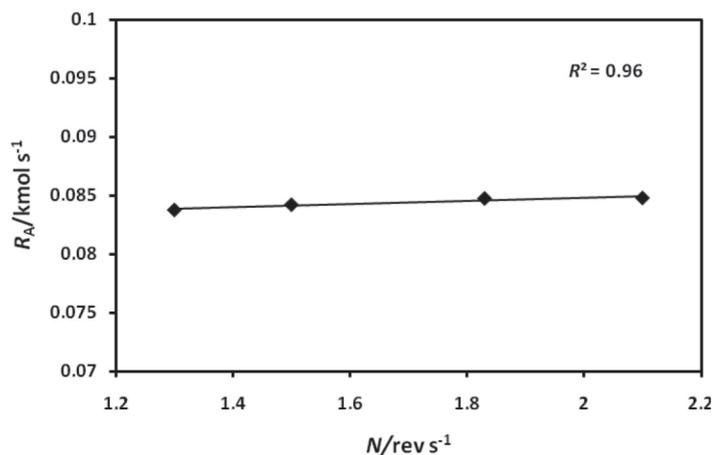


Fig. 6 – Effect of agitation speed on the specific rate of extraction for the reactive extraction of citric acid (0.8 kmol m^{-3}) using $0.114 \text{ kmol m}^{-3}$ TOA in MIBK

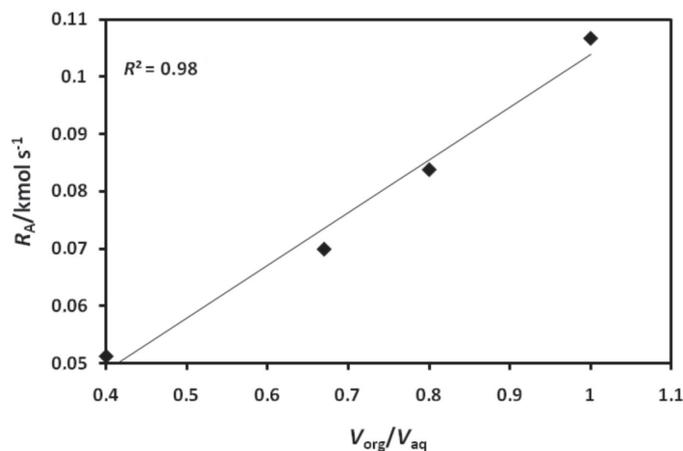


Fig. 7 – Effect of volume ratio of the phases on the specific rate of extraction for the reactive extraction of citric acid (0.8 kmol m^{-3}) using $0.114 \text{ kmol m}^{-3}$ TOA in MIBK

the speed of agitation (1.30 rev s^{-1}), and varying the volume ratio of the organic to aqueous phase from 0.54 to 1. It can be seen in Fig. 7 that the volume ratio of the phases is directly proportional to the specific rate of extraction for the reactive extraction of citric acid with TOA in MIBK.

Regime of extraction accompanied by chemical reaction

Results of preliminary studies conducted in order to discern the regime of extraction reaction of citric acid using TOA in MIBK confirm that the specific rate of extraction, R_A , is directly proportional to initial acid concentration and volume phase ratio ($V_{\text{org}}/V_{\text{aq}}$) (Fig. 7); and is unaffected by the speed of agitation, N (Fig. 6). Thus, with reference to discerning the mechanism, it can be concluded that the extraction reaction between citric acid and TOA in MIBK falls into Regime 1 that is a very slow reaction. The governing equation for the rate of chemical reaction in this regime is as given in Eq. 20:¹⁷

$$R_A = lk_{mn} [\text{H}_3\text{A}]^m [E^o]^n \quad (20)$$

where, m and n are the orders of the reaction with respect to acid and extractant, respectively. k_{mn} is the rate constant for a m^{th} and n^{th} order reaction. The proportionality constant l represents the liquid hold-up.

Order of the extraction reaction

The effect of the reactants concentration on the specific rate of extraction was investigated by keeping the concentration of one of the reactants constant, and varying the other at a fixed speed of agitation (1.30 rev s^{-1}) and the volume ratio of phases (1:1). The initial concentration of TOA was varied

between $0.114 \text{ kmol m}^{-3}$ to $0.457 \text{ kmol m}^{-3}$, while that of equilibrium concentration of citric acid was varied from $0.2 - 0.8 \text{ kmol m}^{-3}$.

Fig. 8 and Fig. 9 depict the variation of specific rate of extraction, R_A with the initial extractant (TOA) concentration ($[E^o]$) in the organic phase and initial concentration of citric acid ($[\text{H}_3\text{A}]_{\text{aq}}$) in the aqueous phase, respectively. Using the method of least squares, based on a linear approximation, the reaction was found to be first order with respect to both the reactants, citric acid and TOA. Replacing the values of m and n ($m = n = 1$), Eq. 20 simplifies to Eq. 21

$$R_A = lk_2 [\text{H}_3\text{A}] [E^o] \quad (21)$$

Specific reaction rate constant

Using Eq. 21, from the slope of Fig. 10, second order rate constant, k_2 , was estimated to be $0.0351 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$, which is in close agreement with the value reported by Nikhade *et al.*¹⁰ ($0.013 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$) for citric acid extraction using Alamine 336 diluted in MIBK. According to Doraiswamy and Sharma,²⁰ for the validity of Regime 1, condition as given by Eq. 16 must be satisfied. For the present case, the extraction reaction falls into the regime that corresponds to a very slow reaction occurring in the bulk with no reaction at the diffusion film.²⁰

Process optimization using differential evolution

The model equation (Eq. 6) correlating distribution coefficient (K_D) to the equilibrium constant (K_E) and stoichiometry of the acid:extractant complex (m, n) was solved using differential evolution optimization technique. The optimized values of m , n , and the equilibrium complexation constants (K_E) are presented in Table 2. Model equation (Eq. 6)

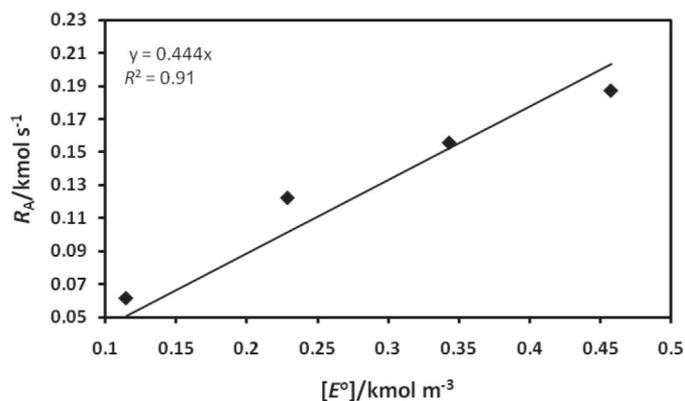


Fig. 8 – Effect of TOA concentration (0.114 to 0.457 kmol m⁻³) on the specific rate of extraction for reactive extraction of citric acid (0.4 kmol m⁻³)

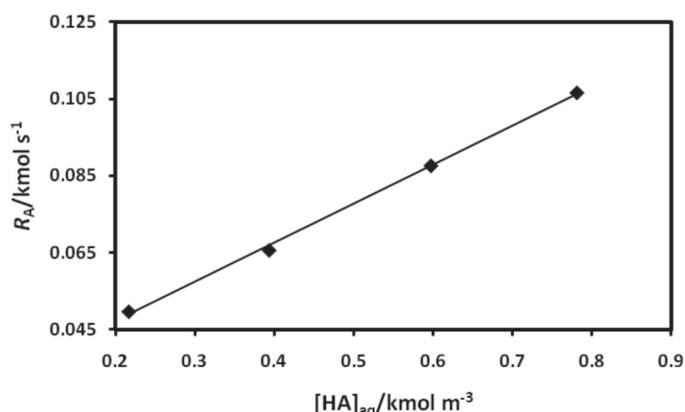


Fig. 9 – Effect of initial acid concentration on specific rate of extraction for reactive extraction of citric acid with TOA (0.114 kmol m⁻³) diluted in MIBK

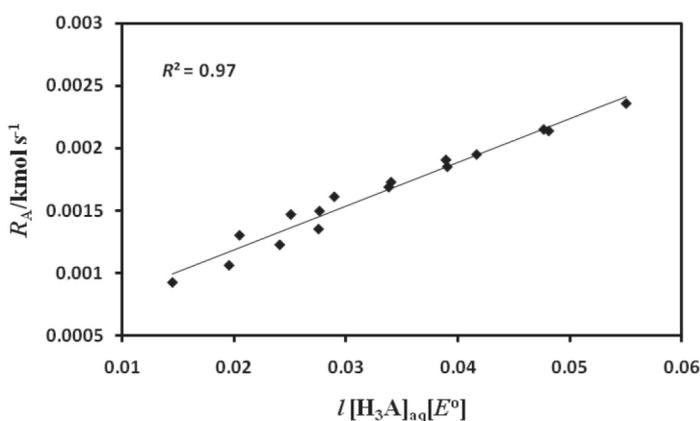


Fig. 10 – Estimation of the second order rate constant for the reaction between citric acid and TOA in MIBK

was used for the calculation of corresponding model values of K_D , based on the optimized values. The predicted values of K_D for each extraction system using DE approach shows a good resemblance with the experimental values of K_D . In the extraction of citric acid using TBP, TOA, and A336, the predicted

Table 2 – Optimum values of K_E , m and n estimated using differential evolution for reactive extraction of citric acid using different extractants (TOA/TBP/A336) in MIBK

Extraction system	K_E (m ³ kmol ⁻¹) ²	m	n	SE ^{a)}
20 % TOA+MIBK	3627.2	2.0000	1	1.0000
30 % A336+MIBK	1.0134	1.1635	1	0.0001
30 % TBP+MIBK	0.3062	0.9555	1	0.0000

a) SE: Standard Error

values of K_D show a slight deviation from experimental values of K_D at lower acid concentrations. This may be due to the precision in the measurement of the very low concentration during experimental analysis when very low initial acid concentration was used. Applying the above strategy, a computer program using MATLAB[®]7.1 was generated and the optimized values were obtained.

At higher concentrations of TOA, the extraction of citric acid was very high. Consequently, the concentration of aqueous phase acid left was very low. Thus, error in measurement of low acid concentration resulted in a significant deviation between model values and experimental values of K_D , particularly in the case of TOA as compared to TBP and A336. In the case of extraction of citric acid using TOA, the higher strength of the complex solvation was found for all the diluents as the K_E values were found to be extremely high (Table 2). A higher affinity of tertiary amine group towards carboxylic acid favors the stable acid:amine complex and a high forward reaction rate result in a higher K_E values (3627.2 (m³ kmol⁻¹)²) for TOA.⁸ This also promoted the higher extractant loading emphasizing the formation of (2:1) acid-amine complex. The FT-IR spectroscopic evidence for the overloading of amine is given in our previous work.¹⁴ Note that the same phenomenon was also observed for quaternary amine, i.e., A336, for which the loading ratio was greater than unity ($m = 1.1635$). However, A336 was not much efficient compared to TOA due to the steric hindrance. Whereas, the overloading in the case of phosphate bearing extractants was totally absent which was reflected from the loading value for TBP, i.e. $m = 0.9555$, that was less than unity. The formation of acid:amine complexes also depended on the nature of diluents, which affect the basicity of the amine and the stability of the ion pair formed in the extract phase. The synergistic extraction strength of the TOA+MIBK system was remarkably high due to the simultaneous effect of the physical extraction in addition to chemical interaction through hydrogen bonding.^{21–23} MIBK affected the diluent complex aggregation more readily through hydrogen bonding and dipole-dipole inter-

action than the amine-free diluent-acid association. These results envisage that the diluents are involved not only in the physical extraction, but also enhance the polarity of extractant.

Conclusions

Extraction equilibria of citric acid using three different extractants, TBP, TOA and A336 in MIBK have been studied. Among all extraction systems, TOA in MIBK has been observed to be the most efficient, enabling ~92 % ($K_{D,avg} = 11.74$) extraction of citric acid from aqueous solutions. Kinetic studies provided that the citric acid-TOA complexation reaction fall under the very slow reaction regime with overall second order rate constant of $0.0351 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$. Only (1:1) stoichiometry of acid-extractant complex was observed with both A336 and TBP in MIBK with $K_{E1} = 1.405 \text{ m}^3 \text{ kmol}^{-1}$ and $0.154 \text{ m}^3 \text{ kmol}^{-1}$ respectively, while (2:1) complex was observed with TOA in MIBK with $K_{E2} = 3715.1 \text{ (m}^3 \text{ kmol}^{-1})^2$. The analogous results are found with the mathematical model, optimized by differential evolution technique. The findings of the present study are useful in the design and development of extraction equipment.

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Nomenclature

A_C	– Cross-sectional area of stirred tank, m^2
K_a	– Citric acid dissociation constant, $(\text{kmol m}^{-3})^3$
K_D	– Distribution coefficient, –
K_E	– Overall equilibrium complexation constant, –
K_{E1}	– (1:1) acid-extractant equilibrium complexation constant, $\text{m}^3 \text{ kmol}^{-1}$
K_{E2}	– (2:1) acid-extractant equilibrium complexation constant, $(\text{m}^3 \text{ kmol}^{-1})^2$
k_{mn}	– Reaction rate constant: $(m+n)^{\text{th}}$ order, $(\text{m}^3 \text{ kmol}^{-1})^{m+R-1} \text{ s}^{-1}$
l	– Liquid holdup, –
m	– Number of acid molecules in complex, –
n	– Number of extractant molecules in complex, –
R_A	– Reaction rate, $\text{kmol m}^{-3} \text{ s}^{-1}$
V_{aq}	– Aqueous phase volume, m^3
V_{org}	– Organic phase volume, m^3
Z	– Loading ratio, –

Z_m	– Modified loading ratio, –
μ	– Acid taken by diluent alone per unit extractant concentration, –
v	– Diluent's fraction in organic phase, –

Abbreviations

$[E]$	– Extractant concentration, kmol m^{-3}
$[H_3A]$	– Citric acid concentration, kmol m^{-3}
$[(H_3A)_m \cdot E_n]$	– Citric acid-extractant complex, kmol m^{-3}
TOA	– Tri- <i>n</i> -octylamine
TBP	– Tri- <i>n</i> -butylphosphate
A336	– Aliquat 336

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