



Equilibrium studies of aconitic acid extraction using tri-*n*-octyl amine (TOA) as extractant

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Conventionally, aconitic acid (AA) is extracted from natural resources like molasses (sugar cane), red beet etc. However, to meet the ever increasing demand of AA for use in biopolymer, surfactants and in drugs, an alternative way is needed which is economical as well as eco-friendly. Fermentation is an alternative route for the production of AA to meet industrial demand. But, it is very challenging to separate AA from fermenter. Out of different techniques available to separate carboxylic acids from fermentation broth; reactive extraction is found highly suitable. Nevertheless, for higher selectivity and effective acid recovery using extraction, investigation on efficiency of extraction systems (diluent and extractants) is highly desired. In this work, equilibrium studies of reactive extraction of *trans*-aconitic acid (TAA) from aqueous solutions with different diluents (cyclohexanone, MIBK, benzene, and *n*-heptane) with tri-*n*-octyl amine (TOA) as an extractant was performed. Using the above extraction systems with different initial acid concentrations and vol% of extractants, distribution coefficients (K_D) were evaluated. Also, effect of initial acid concentration and effect of diluents on extraction efficiency (E) of TAA was studied. Extraction efficiency of (benzene + TOA) diluent system is found highest. Besides that extraction efficiency was found independent on phase volume ratio when TOA was used as extractant.

Keywords: Reactive extraction, *trans*-aconitic acid, distribution coefficient, extraction efficiency, tri-*n*-octyl amine.

Introduction

Trans-aconitic acid (TAA) is a tri-carboxylic acid having multifarious uses. Demand of aconitic acid is ever increasing due to its use in food industry as acidulant, in polymers as a plasticizers substitute of toxic plasticizers and also in medicinal applications as neuro drugs. Source of the aconitic acid is either natural or synthetic. Continuous commercial production through natural source is not feasible due to seasonal crops. We can't depend on traditional chemical pathways due to constant increase of fossil fuel's prices and involvement of many harsh chemicals which makes it non eco-friendly and uneconomical. Bio-route is the potential alternative to produce carboxylic acids economically to meet industrial demands¹. Fermentation or bioprocess is the best replacement for the commercial production of TAA to meet demand of industries in an economical way. Microorganisms employed to produce *trans*-aconitic acid from fermentation route are *A. terreus*, *A. itaconicus* and *E. coli*²⁻⁴. It is very difficult to recover the TAA from the fermenter. However, gen-

erally methods used to separate carboxylic acids from fermenter are: chemical precipitation, adsorption, distillation, extraction, ion-exchange and membrane separations (reverse osmosis, micro and ultra-filtrations) etc^{5,6}. Among these existing techniques some involved hazardous chemicals, some are energy intensive, and few are still at R & D stage and costly. Overall, extraction is the best among them to recover carboxylic acids from the fermenter continuously. Extraction is mainly two type's physical and reactive extraction. Renge *et al.* studied equilibrium (physical) for *trans*-aconitic acid using diluents like alcohols *n*-butanol and 1-decanol⁶. Azzam and Radwan, reported extraction of aconitic acid using ethylacetate and recovery factor is 90%⁷.

In the present work, recovery of *trans*-aconitic acid (TAA) from aqueous phase using extractant; tertiary amine (TOA) with active diluents: ketone group (cyclohexanone and MIBK) and inactive hydrocarbon diluents (benzene and *n*-heptanes) was studied using reactive extraction. Also effect of diluents volume or organic phase volume on distribution coefficient

of TAA was investigated. The extraction (reactive) equilibrium was analysed in terms of distribution coefficient (K_D) and percentage of extraction efficiency (%*E*).

Materials and methods

Materials:

Aqueous phase was prepared by diluting *trans*-aconitic acid in Millipore water. For this study tri-*n*-octyl amine (TOA) is used as extractant. *trans*-Aconitic acid, tri-*n*-butyl phosphate (TBP; 99% assay) and diluents used *n*-heptane, benzene, cyclohexanone and methyl-iso-butyl-ketone (MIBK) was procure from Loba Chemie Pvt. Ltd., Mumbai, India. Fisher scientific manufactured sodium hydroxide (NaOH) was used for titration. Qualigens fine chemicals product, oxalic acid (99.5% assays) is considered for standardization of NaOH. Phenolphthalein indicator with pH range 8–10 was obtained from Fisher scientific. Utilized, analytical grade reagents without any modification.

Methods:

Experiments of equilibrium studies⁸, were carried out by taking equal volumes of 10 ml of aqueous phase and diluents phase taken in 50 ml conical flask and shaken for 2 h at fixed temperature 300.15 K at moderate shaking speed in a water bath shaker (REMI RSB-12). Settling time for equilibrium mixture was fixed to 1 h. A micro pipette was used to take 2 ml sample from aqueous phase for concentration measurement. Conventional acid base titration method was used to evaluate acid concentration in aqueous phase with 0.01 *N* NaOH.

Results and discussion

Reactive extraction:

Extraction is an indirect mass transfer operation to separate component of interest from feed phase using immiscible solvent phase. Diluents (solvents) extracts the desired component based upon dipole induced dipole attraction (London dispersion forces) or ion-ion interactions. Additionally, there is reactant or extractant present in the organic phase which helps to make complex and it is known as reactive extraction. Generally, three types of diluents (organic solvents) used in extraction are hydrocarbon solvents (inactive) and other two are known as active diluents (oxygenated and

halogenated) solvents. In present study, active diluents chosen are oxygenated hydrocarbon solvents such as ketone group diluents (cyclohexanone and MIBK) and inactive diluents such as benzene, *n*-heptane; which primarily extracts acid by ion-pair interactions or through hydrogen bonding⁹.

Experiments were conducted to investigate the reactive extraction equilibrium between aqueous and organic phases. Equilibrium studies and corresponding extraction isotherms for *trans*-aconitic acid using active diluents and inactive diluents to evaluate the extraction efficiency are shown in Fig. 1. Interpretation of experimental results shows that the highest distribution coefficient (K_D) for *trans*-aconitic acid is obtained with MIBK and benzene. A comparison of present study with our previous studies on recovery of *trans*-aconitic acid using reactive extraction with TBP as extractant with same diluents¹⁰ is shown in Fig. 4. The obtained results with TOA are much better than the TBP as extractant. This is mainly due to difference in extraction efficiency of extractant than diluents. Hydrogen bonding is the reason for formation of complex between the extractant (TOA and TBP) and *trans*-aconitic acid. Hydrogen bonding is physical attraction between carboxylic group of the acid and the extractant. Based on Lewis basicity effect, extractant TOA is more basic in nature than the TBP (less basic). Therefore, affiliation of acid with TOA is much stronger than TBP extractant resulting higher extraction efficiency (%*E*). Because of the strong affiliation between acid and TOA (extractant), the influence of the diluents properties is reduced. Whereas, it is reverse in case of TBP even though it is giving higher extraction efficiency than physical extraction the extraction efficiency follows properties of the diluents⁸.

Effect of diluents volume:

Experiments were carried out to examine the influence of extractants and diluents on extraction efficiency. This investigation was done by changing phase volume ratio ($V_\alpha:V_\beta$) i.e. volume of aqueous phase (α -phase) to volume of diluent phase (β -phase) for all diluents keeping extractant concentration constant (1,2,3) in one case and varying the extractant concentration (1,1,1) in another case. The results were obtained for phase volume ratio ($V_\alpha:V_\beta$): (10:10), (10:20) and (10:30) for (TOA + diluents) system, which shows there are

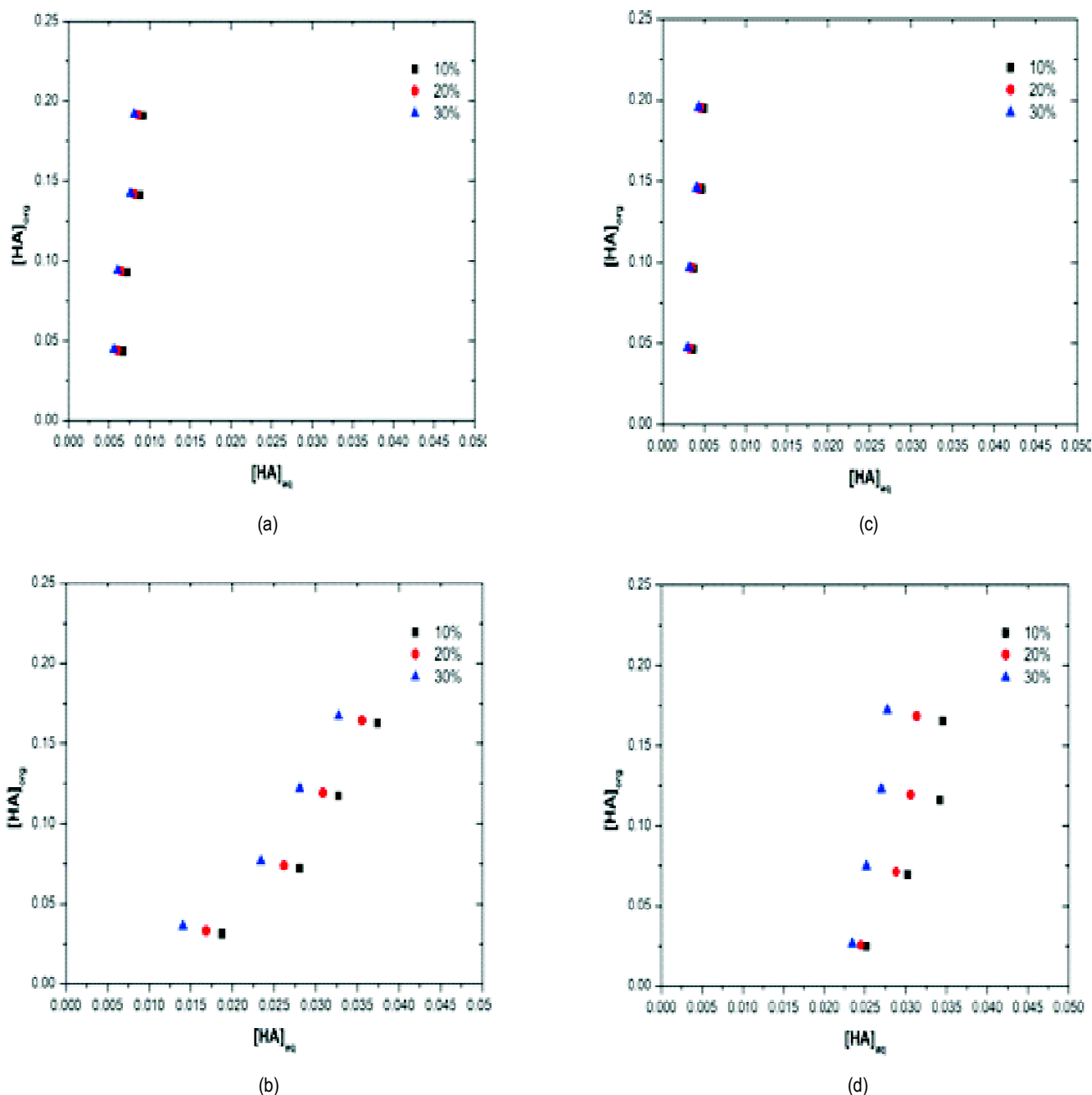


Fig. 1. Equilibrium isotherms of *trans*-aconitic acid using different diluents with extractant; TOA concentration (10, 20 and 30 v/v): (a) MIBK, (b) cyclohexanone, (c) benzene and (d) *n*-heptane.

no change in the extraction efficiency with increasing diluents phase (β -phase) volume as shown in Fig. 2. This is due to strong interaction between *trans*-aconitic acid (HA) with TOA at equal volume of phases (i.e. (10:10)) which provided maximum extraction efficiency. This indicates, sufficient surface area is available for maximum complex formations between

trans-aconitic acid (HA) with TOA for a given volume of diluents (β -phase)¹¹ and beyond (10:10) phase volume ratio (i.e. (10:20) and (10:30)) there is no change in extraction efficiency. Extraction efficiency of (TBP + diluents) system is showing increase with increasing volume of diluents phases (β -phase) as shown in Fig. 3. This may be attributed to weak

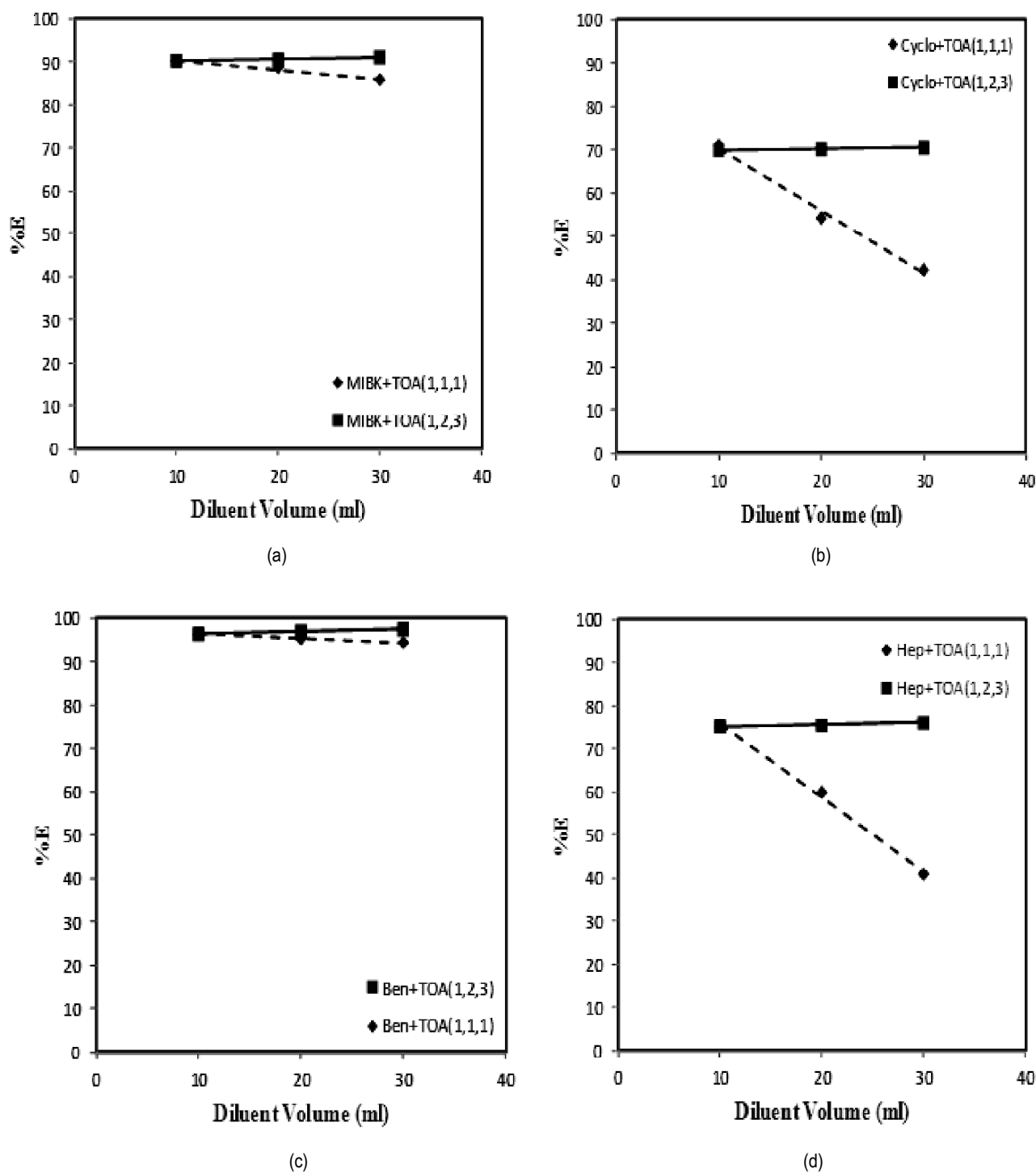


Fig. 2. Effect of phase volume ratio (i.e. (1,1), (1,2) and (1,3)) on extraction efficiency for different diluents with TOA as extractant: (a) MIBK, (b) cyclohexanone, (c) benzene and (d) *n*-heptane.

interaction between *trans*-aconitic acid (HA) with TBP at equal volume of phases (i.e. (10:10)) as surface available per unit

volume of diluent is not enough and the extraction efficiency is minimum.

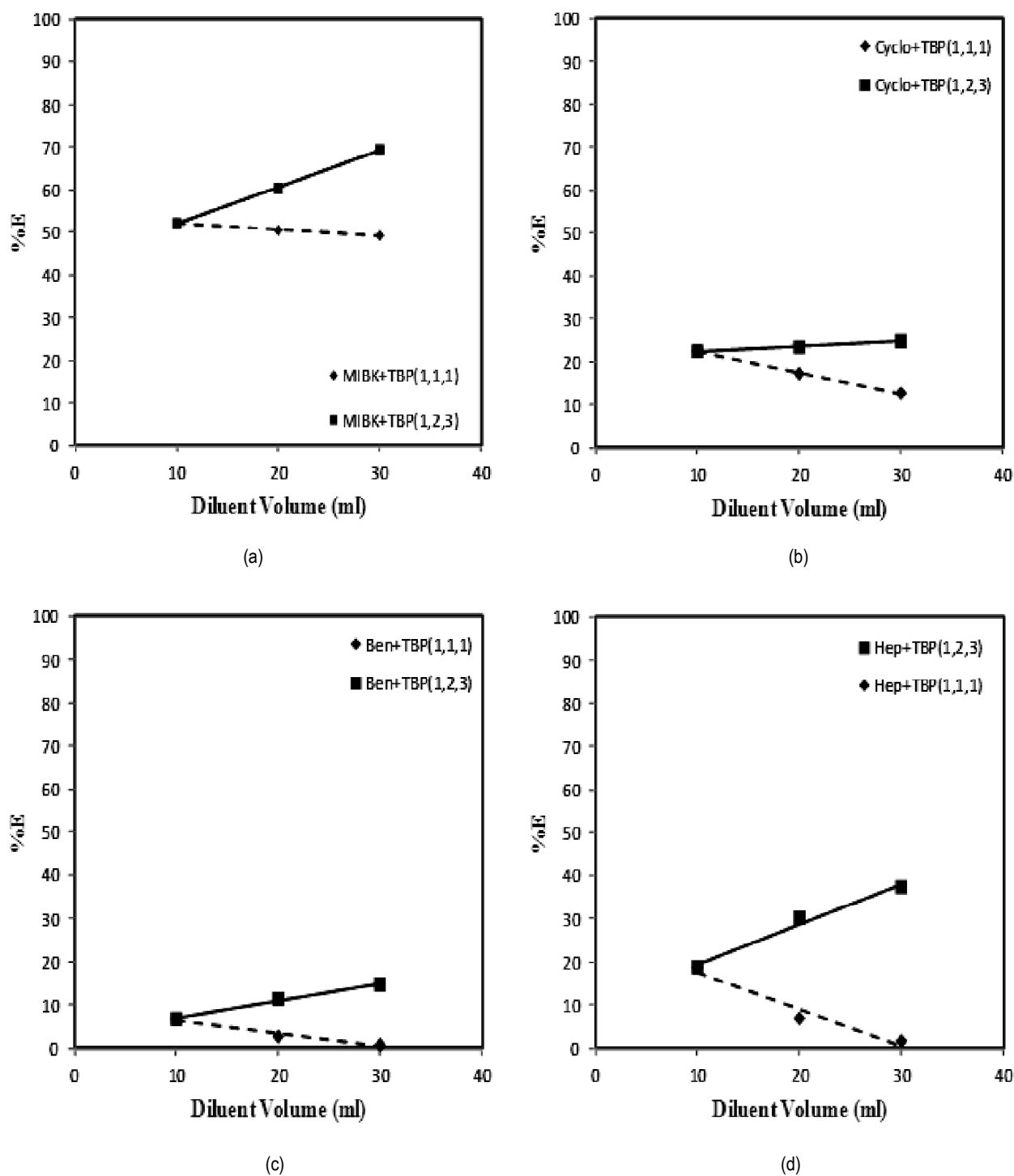


Fig. 3. Effect of phase volume ratio (i.e. (1,1), (1,2) and (1,3)) on extraction efficiency for different diluents with TBP as extractant: (a) MIBK, (b) cyclohexanone, (c) benzene and (d) *n*-heptane.

Note: Abscissa of the Figs. 2 and 3 is representing varying diluent phase volume (β -phase) to the constant aqueous phase volume (β -phase) which is 10 ml.

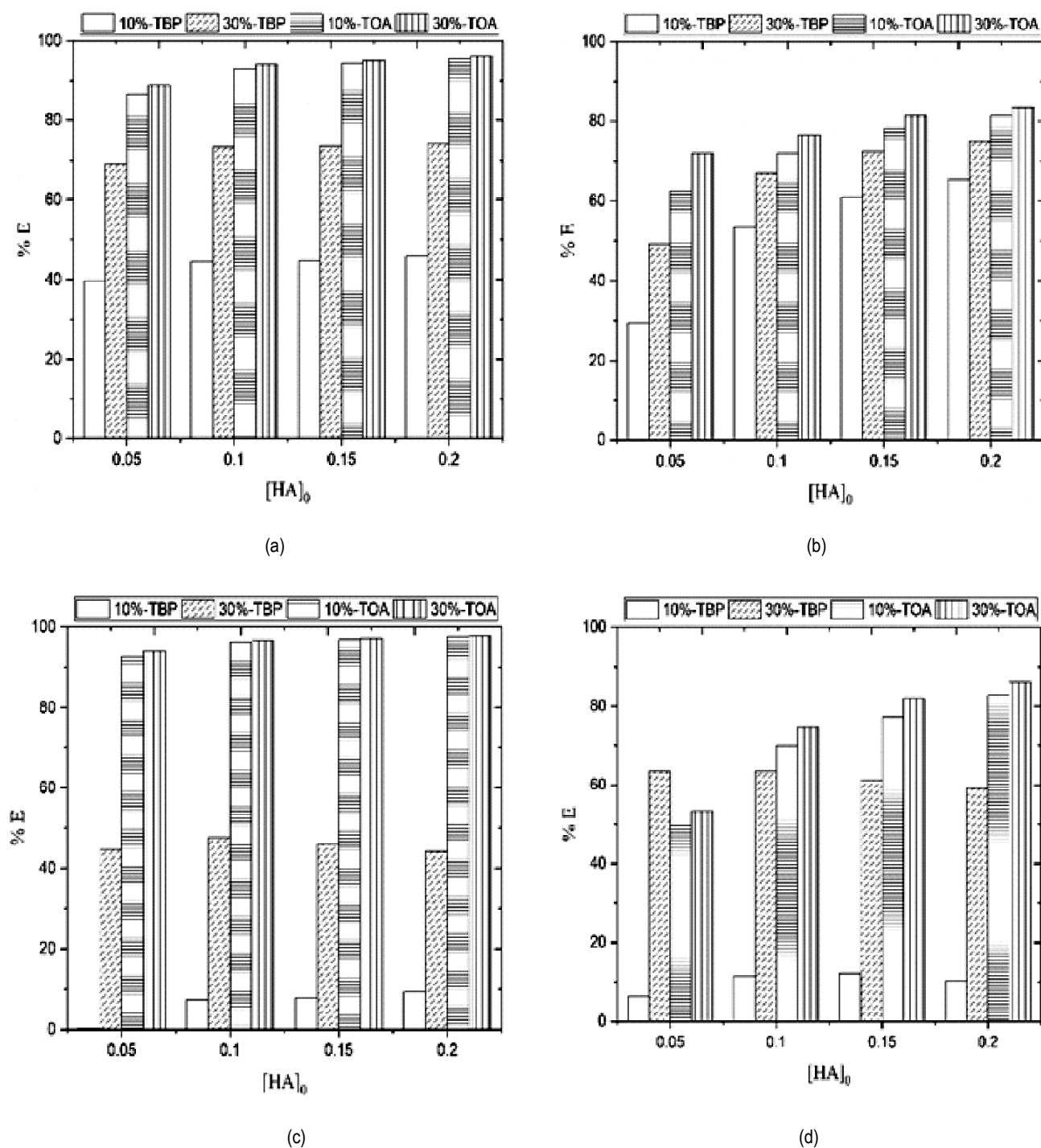


Fig. 4. Comparison of extraction efficiency of *trans*-aconitic acid [0.05, 0.10, 0.15 and 0.20 Kmole.m⁻³] using different diluents with TOA and TBP extractant: (a) MIBK, (b) cyclohexanone, (c) benzene and (d) *n*-heptane.

Conclusions

Trans-aconitic acid recovery using reactive extraction from aqueous solutions with tri-*n*-octyl amine (TOA) as an extractant and four diluents (cyclohexanone, MIBK, benzene and *n*-heptane) were carried out. Distribution coefficients were evaluated for different extraction systems with different initial acid concentrations and vol% of extractants. Extraction efficiency of (benzene + TOA) extraction system is higher than (MIBK + TOA), (cyclohexanone + TOA) and (*n*-heptane + TOA) systems. It was also, observed that, in case of TOA as extractant, extraction efficiency is independent on phase volume ratio (diluents phase volume to the aqueous phase volume).

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