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Study on Extraction of Carboxylic Acid Using Solvent Extraction

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Abstract: *Liquid–liquid extraction is an economical, efficient, and environment-friendly benign method for the separation of dilute solutions, including carboxylic acids, amino acids, amines, phenols, etc. This process of extraction is attractive if an adequate solvent is used, which shows high selectivity and efficiency, does not affect the thermal stability of products, and requires low energy consumption. The carboxylic acid especially phthalic acid and citric acid is mainly occurs in the effluent streams from pharmaceutical, paints and food industries. In present work, removal of Phthalic acid and citric acid from aqueous phase using liquid-liquid extraction has been investigated. Tri-butyl phosphate (TBP) and Tri-octyl amine (TOA) and kerosene/ 1-Dodecanol were used as extractant and diluents for the experiments. Effect of several parameters such as feed concentration, extractant concentration, and diluents concentration etc. has been studied. The effect of initial concentration of phthalic acid in aqueous feed was studied and the results showed that the extraction and thereby* K_D *values were found to be increased with increase in initial feed concentration. Effect of different organic extractants on extraction performance of citric acid was studied and it showed that the extraction performance was higher with the extractant TOA /kerosene as compared to TBP /kerosene and TBP/1-Dodeacanol.*

Keywords: *Extraction, Phthalic acid, citric acid, TBP, TOA, Kerosene, 1-Dodecanol, equilibrium.*

1. Introduction:

Certain carboxylic acids have a variety of applications in industries producing food and pharmaceutical products, biotechnical industries, surfactants, detergents, and green solvents. Currently, carboxylic acids have become interesting as a raw material for biodegradable polymers. And due to this rising demand, the large volume production of carboxylic acids has been the focus of attention. The aim of present work is to select the suitable extractant and diluents for the carboxylic acid recovery from dilute aqueous solutions and to determine the equilibrium extraction constant.

A carboxylic acid is an organic compound that contains a carboxyl group (COOH). The general formula of a carboxylic acid is R–COOH, with R referring to the rest of the (possibly quite large) molecule. Carboxylic acids occur widely and include the amino acids (which make up proteins) and acetic acid (which is part of vinegar and occurs in metabolism).In waste water, many acids were present such as formic acid, propionic acid, acetic acid, butyric acid, lactic acid, phthalic acid. Many acids can cause problem to eco and human system such as lethal effects, excessive skin problems, cramping, cancers, ligament problems and also it interfere in ability of aquatic living organisms to take oxygen, salt, nutrients. In the present study, phthalic acid and citric acid have been selected for separation study.

Phthalic acid is an aromatic di-carboxylic acid, with formula $C_6H_4\ (CO_2H)_2$. Phthalic acid is used mainly in the form of the anhydride to produce other chemicals such as dyes, perfumes, saccharin, phthalates and many other useful products. Phthalic acid is an isomer of iso-phthalic acid and tere-phthalic acid. Although phthalic acid is of modest commercial importance, the closely related derivative phthalic anhydride is a commodity chemical produced on a large scale. Phthalic acid, when found in tissues or bio-fluids arises from exposure to these phthalate products. Phthalate is an environmental chemical of heightened public concern because reports of its potential risk to male reproductive health, being significantly associated with reduced sperm concentration to pesticide concentration in men's urine.

Citric acid is a weak organic tri-carboxylic acid having the chemical formula $C_6H_8O_7$. It occurs naturally in citrus fruits. It is a natural preservative/conservative used to add an acidic or sour taste to fluid an drinks. More than a million tons of citric acid is manufactured every year. It is used widely as an acidifier, as flavouring and chelating agent. Citric acid is a natural constituent and common metabolite of plants and animals. It is a versatile organic acid that is utilized in a wide range of industries. It is used as an anti-oxidizing, acidifying, flavouring, preserving, chelating and buffering agent in the food and beverages, pharmaceutical, and cosmetics industries.The pharmaceutical, food, and biotechnology industries abound with examples where there is a need to remove organic compounds from aqueous effluents or fermentation broth. Organo-phosphorus compounds and long chain tertiary amines are effective extractants to recover and separate organic acids from dilute solutions.

The recovery of organic acids such as citric acid, lactic acid, levulinic acid etc. from aqueous solutions is an industrially important separation process, especially because of their low concentration in the fermentation broths (<10%). The industrial method of recovery of the acid (e.g. Citric acid) involves the precipitation of citric acid as calcium citrate by adding hydrated lime, and treatment with sulphuric acid for citric acid separation. However, this method of recovery is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste. The physical extraction with conventional solvents is not an efficient method for the recovery of these acids becauseof very low distribution coefficients (K_D). Therefore, reactive extraction with specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxyl carboxylic acids. Reactive extraction represents a joint between the chemical phenomena (the reaction between the solute and extractant) and physical phenomena (diffusion and solubilization of the compound resulted from the chemical reaction). Organic bases such as tertiary amines offer advantages over other extractants, on the grounds of lower cost and generally higher equilibrium distribution coefficients (K_D).

Many factors have an important influence on the extraction characteristics-the nature of the acid extracted the concentration of the acid and the extractant, and the type of the diluent used. The disposal of waste waters containing most widely-used industrial organic acids such as acetic acid, formic acid, phthalic acid, butyric acid and propionic acid has been recognized as a significant expense to the industry and environment**.**

Liquid–liquid extraction also known as solvent extraction and partitioning, is a method to separate compounds based on their relative solubility in two different immiscible liquids, usually water and an organic solvent. It is an Extraction of a substance from one liquid into another liquid phase.

Normally one of the two phases is an organic phase while the other is an aqueous phase. Under equilibrium conditions the distribution of solute over the two phases is determined by the distribution law. After the extraction the two phases can be separated because of their immiscibility. Component is then separated from the extract phase by a technique such as distillation and the solvent is regenerated. Further extractions may be carried out to remove more components. Liquid-liquid extraction can also be used to remove a component from an organic phase by adding an aqueous phase.Solvent extraction is used in nuclear reprocessing, ore processing, and the production of fine organic compounds, the processing of perfumes, the production of vegetable oils and biodiesel, and other industries.There are different methods for separating acids from waste water such as Fractional distillation, Adsorption, Extraction, Precipitation, Ion exchange, reverse osmosis, Electro dialysis, etc.

Distillation

Water is the lower boiling component and relative volatility of water to carboxylic acid is very low. Although carboxylic acid and water do not form an azeotrope, it is necessary to have a large number of equilibrium stages and a very high reflux ratio to obtain glacial grade acid by simple distillation. As an alternative to fractionation, to reduce energy consumption, azeotropic dehydration can be employed with addition of anther liquid. In this technique, the entrainer carries the water overhead in the distillation column with the mixture being phase separated after condensation and entrainer being returned to the column. It is effective only for high concentration of acids.

Membrane Process

This membrane process include the ability to recover the acids in concentrated form for reuse or more economical disposal of waste, low pressure (ambient) operation, simple scale-up using commercial hollow fiber modules, and ease of in-situ regeneration of the polymeric liquid. The process has shown treatment feasibility for several types of aqueous waste streams, but it is not cost effective. In these processes, the problem of membrane fouling which requires frequent cleaning of the dialyzer. It gives a higher extent of acids separation but with increased power and energy consumption. The drawbacks are being of hindered implementation, mainly complexity of operation and swelling in liquid surfactant membrane. However, supported liquid membrane often suffers from membrane instability.

Adsorption

Carboxylic acids may be recovered by adsorption on solid adsorbent separated carboxylic acid by using a polymer adsorbent of pyridine skeletal structure and a cross-linked structure. The polymer adsorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts. The selected diluents were aliphatic alcohol, aliphatic ketones and carboxylic esters. But the cost associated with regeneration of commercial adsorbents make adsorption operation very expensive.

Precipitation

Precipitation is a process used for the purification of carboxylic acid. In the calcium precipitation process, the separation and final purification stages account for up to 50% of the production costs and produces a large quantity of solid waste. So, Conventional calcium precipitation method is simple and reliable but it is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste.

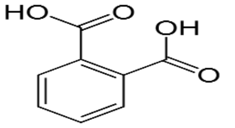
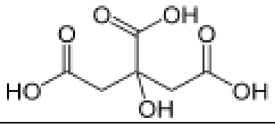
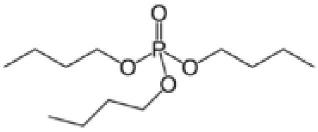
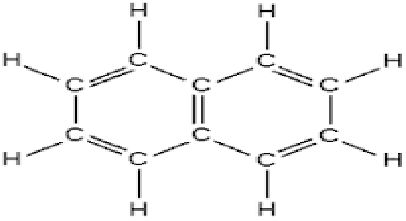
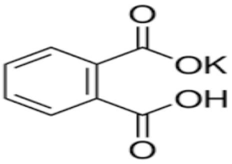
Among these processes, liquid-liquid extraction has had special attention. This process of extraction is attractive if an adequate solvent is used, which shows high selectivity and efficiency, does not affect the thermal stability of products and requires low energy consumption.

2. Materials and methods

3.

The various materials such as acid, solvent, and diluents such as phthalic acid (99% pure), citric acid (99.5% pure), TBP (99% pure), kerosene (low odor), 1-Dodeacanol (98.5% pure), and KHP (potassium hydrogen phthalate) (99% pure) (all are from R and L lab, kharghar) were used for experimentation work. The physical properties of the same are listed below in table 1:

Table 1: physical properties of acid, solvent and diluents.

Chemical	Formula	Structure	Mol.wt.	Density(g/cc)
Phthalic acid	C_6H_4-(COOH)$_2$		166.14	1.593
Citric acid	$C_6H_8O_7$		192.12	1.665
TBP	OP(O(CH2)3CH3)3		266.32	0.98
Kerosene	CH3(CH2)8–16CH		254.3	0.8
1-Dodeacanol	$C_{12}H_{26}O$		186.34	0.83
KHP	$C_8H_5KO_4$		204.22	1.63

Equilibrium Experiments: Equilibrium experiments were performed to study the extractability of the given extractant. The solute containing aqueous phase and the extractant containing organic phase were equilibrated. The solute then distributes itself in two phases as per its distribution constant (K_D). K_D is a measure of amount of solute being extracted in organic phase at equilibrium.

Stoichiometry of the complex formation of TBP and phthalic acid (Zhou and Wei, 2011):

Organic acids, including phthalic acid, exist as dimmers in an organic phase, especially in non-polar solvents such as kerosene as a result of strong intermolecular hydrogen-bonding with two extractant molecules associating with one phthalic acid molecule. The stoichiometry of the TBP and phthalic acid complex formation in the organic phase is determined as follows,

Using the mass action law and neglecting the physical partitioning of phthalic acid between kerosene and water because of its low hydrophobicity (log P = 0.73), the extraction equilibrium for phthalic acid can be written as a reaction between n molecules of phthalic acid (HA) and one molecule of TBP to form a n : 1 complex:

$$nHA + S_{org} \overset{K_{1n}}{\longleftrightarrow} (HA)_nS_{org} (1)$$

Where the organic phase is denoted by the subscript ‘org’, and K1nis the apparent equilibrium constant.

The distribution coefficient, K_D, is defined as the total molar concentration of phthalic acid (all forms) in the organic phase (C_{org}), divided by that in the aqueous phase (C_{aq}) and can be expressed as:

$$K_{1n} = [(HA)_n \cdot S]_{org} / [HA]^n . S_{org} (2)$$

$$S_o = S_{org} + [(HA)_n \cdot S]_{org}$$

$$= S_{org} + K_{1n}[HA]^n . S_{org} = (1 + K_{1n}[HA]^n)S_{org} \quad (3)$$

$$K_D = C_{org}/C_{aq} = n[(HA)_nS]_{org} /C_{aq} (4)$$

$$= nK_{1n} [HA]^n . S_{org}/C_{aq}$$

Aqueous solutions of different molarities of phthalic acid were prepared using distilled water. The solutions of TBP in pure 1-Dodeacanol and kerosene were prepared. Strength of TBP in these solutions was varied from 10% to 50% by weight. The aqueous solutions had concentration between 150 to 2000 ppm. Equal volumes (2 ml) of extractant solution (organic phase) & acid solutions were taken in 8 ml glass bottles. As both the phases are immiscible with each other, two distinct layers of organic and aqueous phases form. Being lighter the upper layer was of organic phase and consequently lower was that of aqueous phase.

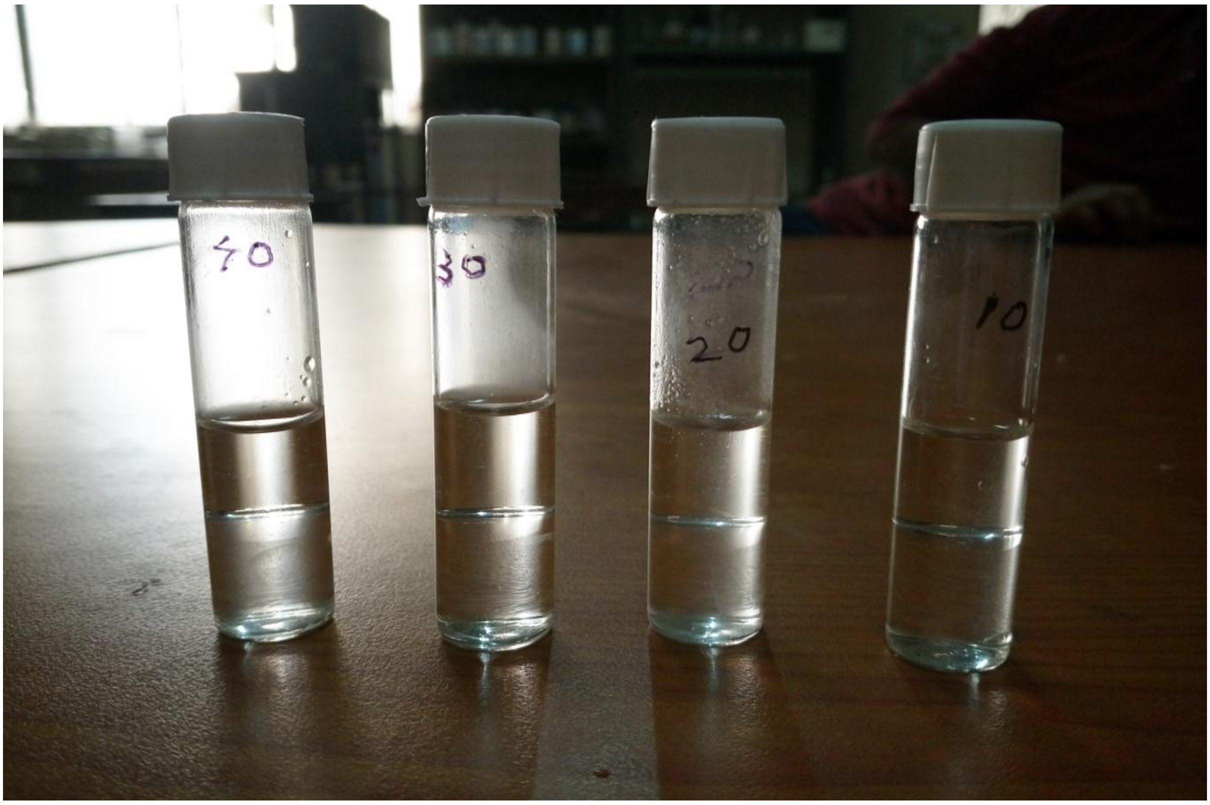


Figure 1: Phthalic acid samples after extraction

To distribute the solute between two phases it is necessary to have intimate contacting of the two phases. So the bottles were then shaken for 30 min to achieve the equilibrium between two phases. After that the bottles were centrifuged at 1000 rpm so as to separate two distinct organic phase & aqueous phases and to remove dispersion if any.

To quantify the amount of phthalic acid in each phase after equilibration, simple acid bas titrations were performed. Very dilute NaOH was used for titrating base with phenolphthalein as indicator. Very dilute solution of NaOH ensured the accuracy in titrations. NaOH solution was standardized by KHP before it was used for titrations. The results are discussed in detail in the later section.

The similar equilibrium experiments were carried out for citric acid using different extractants and diluents such as TBP/Kerosene, TBP/1-Dodeacanol, and TOA/kerosene to investigate the effect of different organic extractants on extraction performance of carboxylic acids. The initial acid concentration of 0.1 M and 50% extractant concentrations was used.

4. Result and Discussion

Equilibrium study:

In this work the equilibrium of liquid-liquid extraction of di carboxylic and tri carboxylic acids from aqueous solutions with organic extractants (TBP and TOA) was investigated. First, the time of extraction to equilibrium was evaluated for each acid. The variation of equilibrium time was in the range 10 to 30 min. the extraction efficiency was found to be better for 30 min. hence 30min was considered as equilibrium time for rest of all experiments.

The equilibrium experiments for acid were conducted for five aqueous solution concentrations, six concentrations of TBP dissolved in kerosene, and six concentrations of a mixture TBP 1-Dodeacanol. The volume ratio of the organic phase to the aqueous solution was 1. The concentration of components was expressed in ppm units (mg/lit).

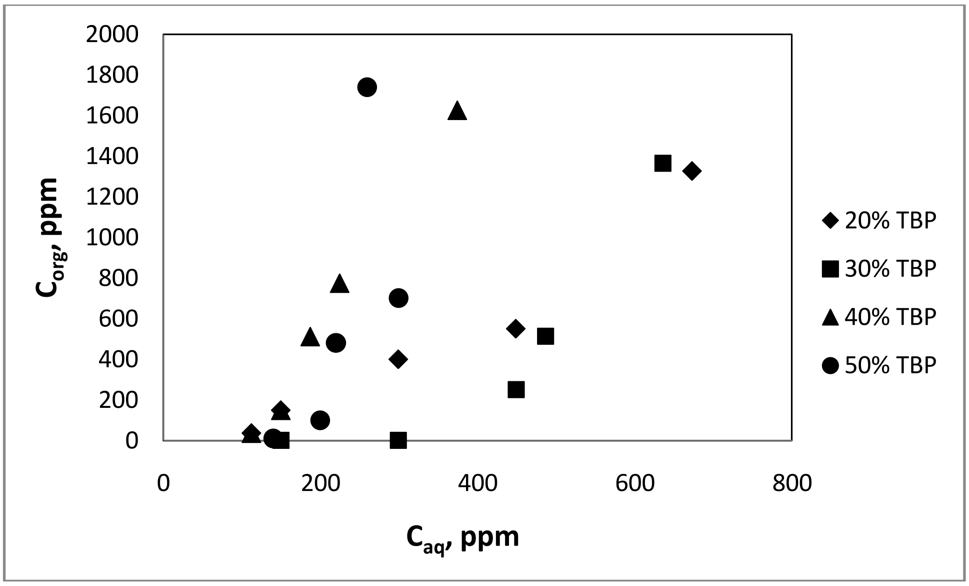


Figure 3: Equilibrium isotherm of phthalic acid using TBP/Kerosene

Figure 3 represent the isotherm of phthalic acid when TBP and kerosene were used as extractant and diluents respectively. The removal of acid from aqueous phase was found to be higher with higher extractant concentration. No extraction was found with 100 % kerosene and 10% of TBP/kerosene.

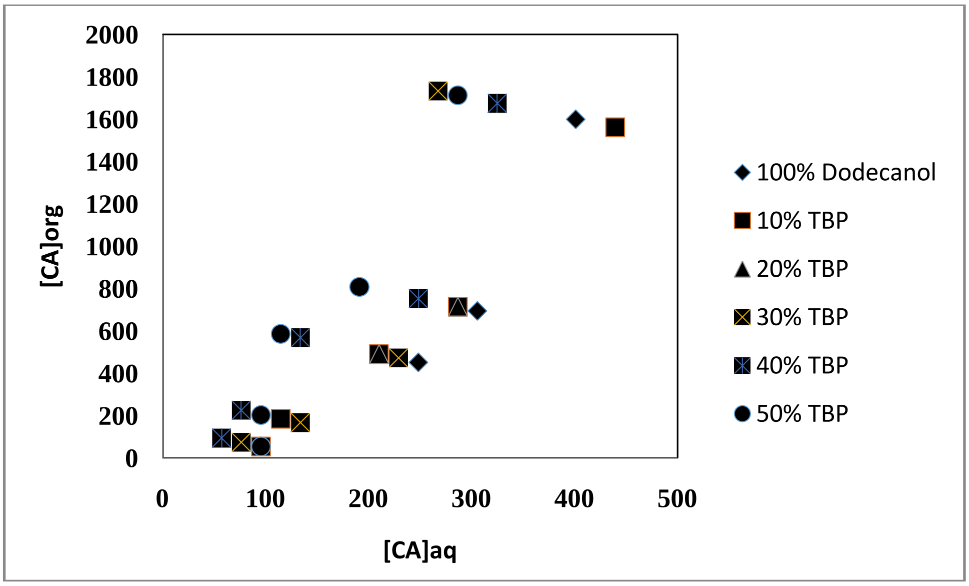


Figure 4: Equilibrium isotherm of phthalic acid with TBP/1-Dodeacanol

Figure 4 shows the isotherm of phthalic acid with TBP/ 1-Dodeacanol as extractant and diluents. Similar to the above study, the removal of acid from aqueous phase was found to be higher with higher extractant concentration.

Effect of extractant concentration on K_D:

The figure represent distribution coefficient of phthalic acid when TBP and kerosene were used as extractant and diluents respectively. Thus, the experimental data showed that when the TBP concentration increases, the distribution coefficient (K_D) also raises. The value for distribution ratio for different extractant and diluents concentration was ranges from 0.003 to 6.71.

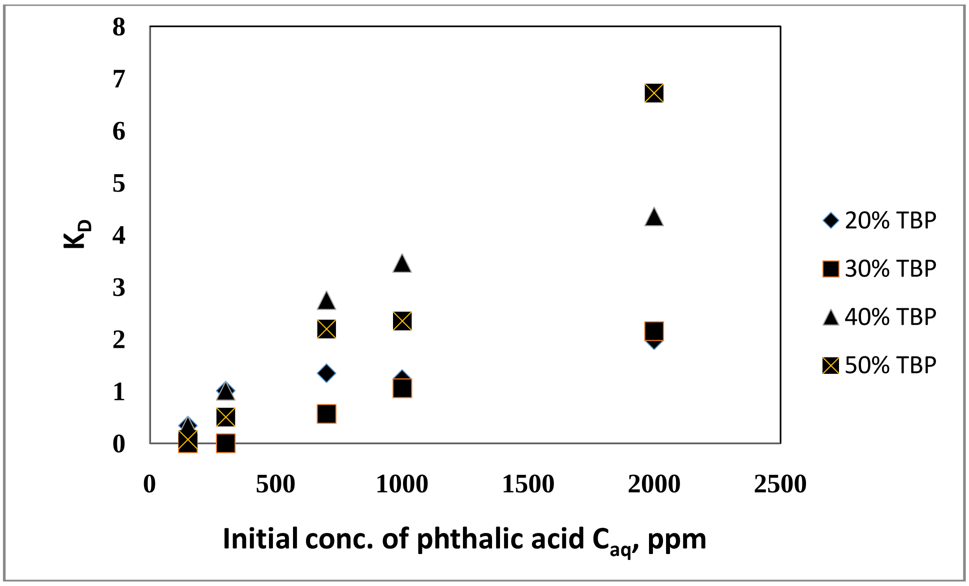


Figure 5: Distribution coefficient vs. initial concentration of acid at different TBP/kerosene concentrations

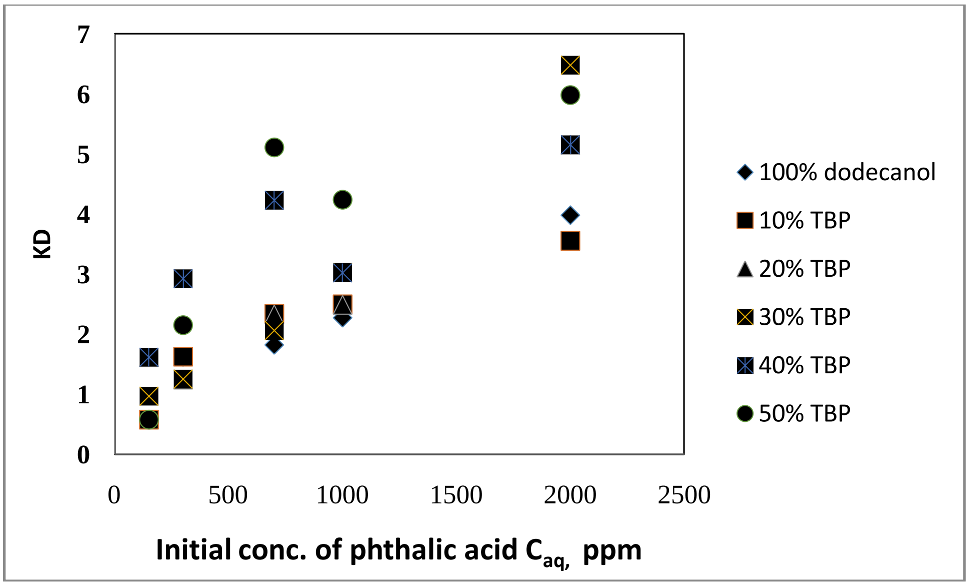


Figure 6: distribution coefficient vs. initial concentration of acid at different TBP/1-Dodeacanol concentrations

In the case of TBP/1-Dodeacanol (figure 6), the experimental data showed the similar effect on the distribution coefficient as above study. The K_D was found to be increased with increase in initial concentration of phthalic acid. But results showed that highest value for K_D at 30% extractant, this might be an experimental error. Distribution coefficient value was greater at 50% of TBP/1-Dodeacanol concentration. The value for distribution coefficient was ranges from 0.5 to 5.97 for different extractant to diluent ratio.

Effect of initial concentration of feed on K_D:

The graph shows the effect of initial feed concentration on K_D. The distribution coefficient for phthalic acid is in the equilibrium aqueous phase acid concentration barely changes as the initial acid concentration increases. The acid concentration in the organic phase, however, increases considerably, and is linear with initial concentration. This implies that different chemical potential–concentration relationships exist in the aqueous and organic phases. The K_D values were found to be increased with increase in initial feed concentration. The values of K_D were inter-related with the extractant concentration.

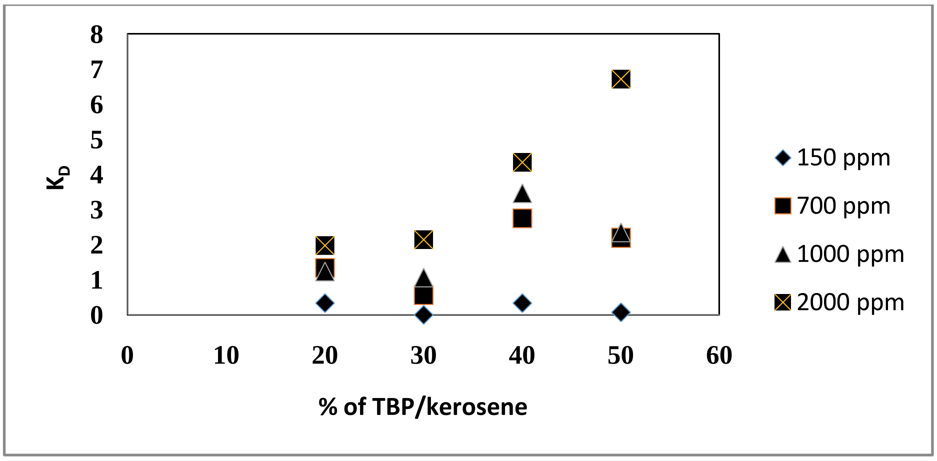


Figure 7 Effect of TBP/Kerosene concentrations on K_D

Figure 7 shows effect of TBP/Kerosene concentration on $K_{D.}$ K_D increases with increase in TBP concentrations as number of molecules of TBP available for complexation increase. Amount of acid molecules taken up by extractant also depends on the stoichiometry of the complexation reaction. The higher K_D values were observed with combined effect of higher feed concentration and higher extractant concentration.K_D values as high as 6.71 can be observed for 50% TBP and 2000 ppm of phthalic acid.

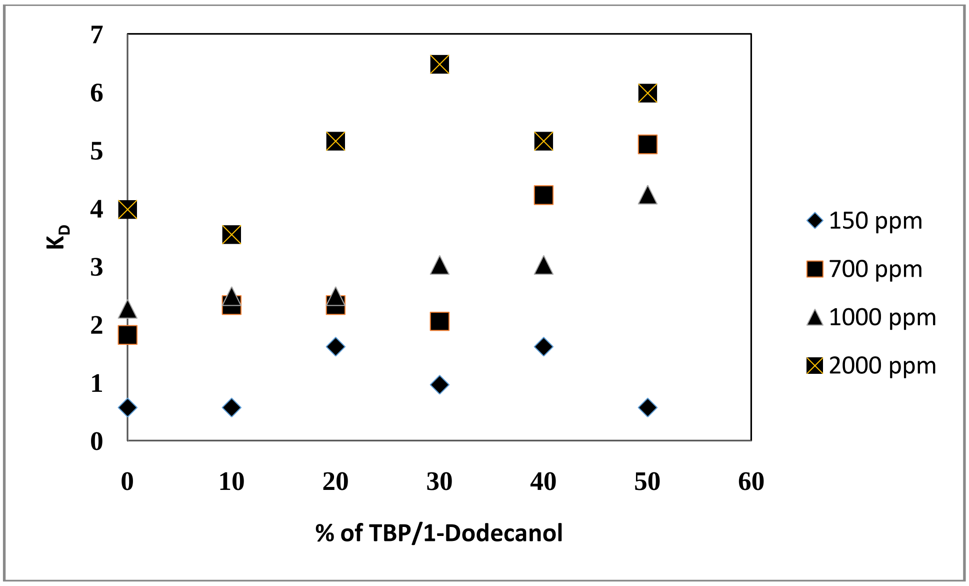


Figure 8: Effect of TBP/1-Dodecanol concentration on K_D

Figure 8 shows effect of TBP/1-Dodecanol concentration on $K_{D.}$ K_D increases with increase in TBP concentrations as number of molecules of TBP available for complexation increase. Amount of acid molecules taken up by extractant also depends on the stoichiometry of the complexation reaction. But results showed that highest value for K_D at 30% this might be an experimental error. K_D values as high as 5.97 can be observed for 50% TBP and 2000 ppm of phthalic acid.

Effect of different organic extractant (study on citric acid):

The equilibrium experiments were carried out to investigate the effect of organic extractants. High-molecular-weight amines are known to be effective extractants for acids and/or metal salts. Due to their physical properties they must always be used in the form of solutions in organic diluents. It has been found that diluents, especially those with functional groups, can affect the extraction behavior of amine significantly. The effect of diluent can be understood in terms of its ability to solvate the organic-phase species; therefore it is necessary to distinguish between the general salvation from electrostatic, dispersion or other forces, and specific salvation due to hydrogen bonding.

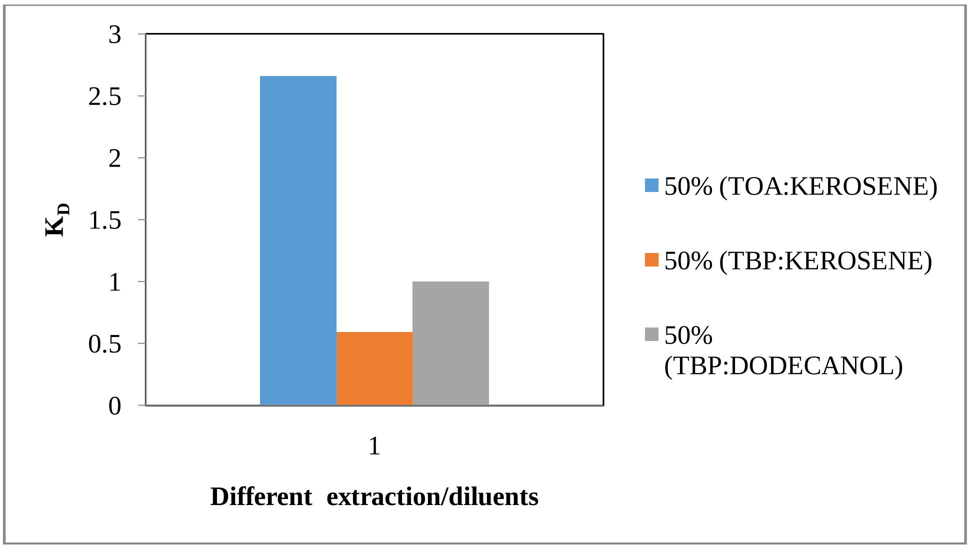


Figure 9: comparison of different extractants and diluents for extraction of citric acid

Extraction of citric acid was found to be higher with 50% (TOA/Kerosene) as compared to that with TBP/kerosene and TBP/1-Dodeacanol. The K_D value of 2.65 was found for TOA/kerosene which shows higher extraction. In general, the selection of the extractant is important for a reactive extraction process. The complexation between the extractant and the solute should also be strong enough to overcome the low activity of the solute in the aqueous phase, yet not so strong as to render regeneration difficult or impossible.

5. Conclusion

Equilibrium study was carried out for phthalic acid and citric acid using different organic extractants like TBP and TOA in kerosene and 1-dodecanol. For phthalic acid study, the equilibrium isotherms showed that the distribution coefficient K_D was found to be increased from 0.003 to 6.97 with increase in TBP extractants concentration with kerosene and 1-Dodeacanol. The extraction was found to be higher with higher TBP concentration (50%) in kerosene and 1-dodecanol. The effect of initial concentration of phthalic acid in aqueous feed was studied and the results showed that the extraction and thereby K_D values were found to be increased with increase in initial feed concentration. For better extraction extractants and solvent selection is more important. Effect of different organic extractants on extraction performance of citric acid was studied and it showed that the extraction performance was higher with the extractant TOA /kerosene as compared to TBP /kerosene and TBP/1-Dodeacanol. The influence of diluents and extractants on the equilibrium extraction is very important and must be taken quantitatively into account for the treatment of the data.

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