

Recovery of Glutaric Acid Using Tri-N-Butyl Phosphate: Effect of Diluents and Temperature

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Abstract

Reactive separation of glutaric acid with tri-n-butyl phosphate in ethyl acetate and hexanol was studied to explain the effect of temperature on the extraction. Extraction was carried out at different temperature range of 308-338 K. The reactive extraction results were discussed in terms of overall distribution coefficients (K_D), degree of extraction ($\eta\%$), loading ratio (ϕ), and equilibrium complexation constants (K_E). The results showed that an increase in temperature reduced distribution coefficients and extraction efficiency for both diluent used in the organic phase. Moreover, thermodynamic function viz enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) were calculated. Reactive extraction of glutaric acid by tri-n-butyl phosphate resulted in negative values of enthalpy. Thus, the reactive extraction process is an exothermic reaction.

Keywords: Reactive extraction; Glutaric acid; Tri-n-butyl phosphate; Ethyl acetate; Hexanol

Introduction

Glutaric acid is a linear di-carboxylic acid. It is produced naturally in the body during the metabolism of amino acids. It is white crystalline solid having the lowest freezing point (371 K) among carboxylic acids and very soluble in water and the solution is a medium strength, i.e., $pK_{a1}=4.31$ and $pK_{a2}=5.41$ [1]. It can be used in production of polymer viz polyester polyols, polyamides, ester plasticizers and corrosion inhibitors, synthesis of pharmaceuticals, surfactants and metal finishing compounds. α -Ketoglutaric acid is a derivative of glutaric acid which can be used in dietary supplement. Current global market value of glutaric acid is approximately US\$ 24000 /year [2]. Despite the immense commercial importance of glutaric acid, it is important to recover from aqueous solution. Glutaric acid can be extract from fermentation medium by calcium salt precipitation but it is very expensive and unfriendly to the environment. The fermented medium contains either the pure acid or its salt or a mixture of both. The search for an advantageous process allowing for the removal of carboxylic acid is based on an approach that removes acids from the fermentation broth or other mixture, while leaving the soluble salts behind in the fermentation broth. Industrial scale fermentors for production of carboxylic acids operate at different temperatures from 273-373 K according to product selectivity [3]. Reactive extraction is an efficient and clean technology for separation of carboxylic acid from fermentation broth and industrial stream. Phosphoric bonded oxygen containing extractants, dissolved in appropriate organic solvents are effective extractants for carboxylic acid [3].

In the present work, equilibrium and thermodynamic study for reactive extraction of glutaric acid has been explored and the result are presented in terms of distribution coefficient, equilibrium complexation constants, loading factor, degree of extraction, thermodynamic function viz. enthalpy, entropy, and Gibbs free energy were calculated.

Materials and Methods

Chemicals

The chemicals used in present work were procured from Merck, India with more than 98% purity whereas glutaric acid purchased from Acros Organics, India. Tri-n-butyl phosphate (TBP) was used as an extractant with ethyl acetate (EA) and hexanol (HX). Physicochemical properties of used chemicals are shown in Table 1. All the chemicals

were used without any further purification.

Experimental procedure

Extraction experiments were conducted in 100 mL Erlenmeyer flasks at various temperatures 308-338 K. The initial aqueous solution of glutaric acid was prepared (0.19-1.10 mol/kg) in deionized water without pH adjustment. An organic solution was prepared by dissolving fix concentration of tri-n-butyl phosphate 1.46 (mol/kg) in ethyl acetate and hexanol. The volumetric ratio of the aqueous and organic phase was kept as 1:1 (15 mL of each phase). The flasks containing the mixture of aqueous and organic solution was shaken for 12 hours in a temperature-controlled water bath shaker RSB-12 (REMI Laboratory Instruments, Mumbai, India) and the solution was allowed to settle for 2-3 hours at room temperature (298 ± 0.5 K) and atmospheric pressure (760 mmHg). The bottom layer (aqueous phase) was used for pH measurement and acid concentration analysis. After equilibrium, the acid concentration of aqueous solution was determined by HPLC. The consistency was checked by repeating few experiments which were observed within the limit of $\pm 2\%$.

Analysis

Analysis was performed with Eclipse XDB-C18 (4.6 mm ID \times 250 mm, 5 μ m) column. Pure acetonitrile (25%) and 20 mM of acetic acid aqueous solution (75%) was used as a mobile phase in volume ratio 1:3 and the flow rate was set at 1 ml/min. Maximum absorption (λ_{max}) of glutaric acid in UV range was observed to be 275 nm thus the detector (DAD) wavelength was set at $\lambda=275$ nm. The column was operated at 308 K with the injection volume of 5 μ L. Before injecting, the samples

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chemicals	MW	MF	BP	MP	S _{water}	ρ	μ	RI	logK _{ow}	D _m
	g/mol		K	K		g/cm ³	cP	η _D		Debye
glutaric acid (pK _{a1} =4.31, pK _{a2} =5.41)	132.12	C ₅ H ₈ O ₄	200°C	98°C	430 g/L	1429	NA	1.4187	-0.47	NA
hexanol	102.17	C ₆ H ₁₄ O	482-432	220- 232	5.9 g/L	0.815	4.37	1.4178	1.858	1.55
ethyl acetate	88.11	C ₄ H ₈ O ₂	350	189	8.3 g/100 ml	0.897	0.43	NA	NA	1.78
tri-n-butyl phosphate	266.31	C ₁₂ H ₂₇ O ₄ P	562	193	1ml/165 ml	0.975	3.8	1.424	2.5-4	NA

MW: molecular weight; MF: molecular formula; BP: boiling point; MP: melting point; S_{water}: solubility in water at 298 K; ρ: density of pure liquid; μ: viscosity; RI: refractive index; log(K_{ow}), water partition coefficient; D_m, dipole moment; NA, not available.

Table 1: Various Physicochemical Properties of Chemicals selected for recovery of Glutaric Acid.

were filtered through syringe filter with pore size 0.2 μm PVD filter media supplied by WHATMAN, U.S.A. Retention time of glutaric acid was 4.3 min. Each analysis was done in triplicates under identical conditions, with the average value of the considered parameters being used. The maximum experimental error was observed as below ± 2 %.

Uncertainty analysis

In this study, experimental uncertainty was evaluated as per the National Institute of Standard and Technology (NIST) protocols [4]. Few experiments were performed in triplicate and the reliability of replicated experiments was found within ± 2% having confidence interval 95%. Standard uncertainty was evaluated to be ± 0.001 by using following Eq.

$$u(x) = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}} \quad (1)$$

Where, x_i=values of experimental observations, \bar{x} =mean of three observations, and N=number of observations. For further calculations average of the replicated data was used.

Results and Discussion

Partition and dimerization coefficient

The physical extraction of glutaric acid with ethyl acetate and hexanol are shown in Figure 1. A linear relationship for equilibrium between organic and aqueous phase of glutaric acid were observed at low range of glutaric acid concentration. At higher concentration of glutaric acid, a parabolic relationship was obtained for all diluents. Henry's law type isotherm can be considered at low concentrations of glutaric acid, while deviation from Henry's law was observed at higher concentrations of glutaric acid where non-ideal behavior was overcome. The values of partition coefficient (P) and dimerization coefficient (D) were obtained by fitting experimental data in the following equation (3):

$$K_D = P + 2DP^2[C_{GA}]_{aq} \quad (2)$$

Where, [C_{GA}]_{aq} concentration of glutaric acid in aqueous solution at equilibrium. Partition and dimerization coefficient values for glutaric acid in ethyl acetate and hexanol was obtained as 0.275, 25.00, and 0.276, 61.92 respectively as shown in Figure 2. Thus, solute-solvent hydrogen bond in comparison to solute-solute bond leads to form dimers.

Distribution coefficient and extraction efficiency

Equation 3 and 4 represents the distribution coefficient (K_D) and extraction efficiency (η%) for glutaric acid and it can be expressed as:

$$K_D = \frac{[C_{GA}]_{org}}{[C_{GA}]_{aq}} \quad (3)$$

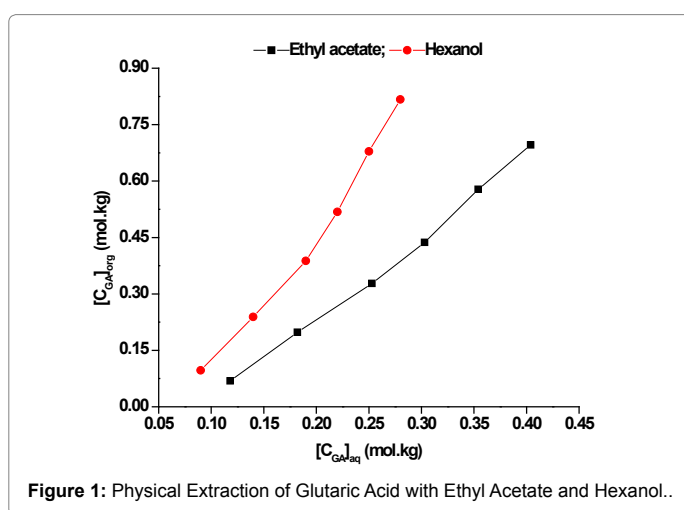


Figure 1: Physical Extraction of Glutaric Acid with Ethyl Acetate and Hexanol.

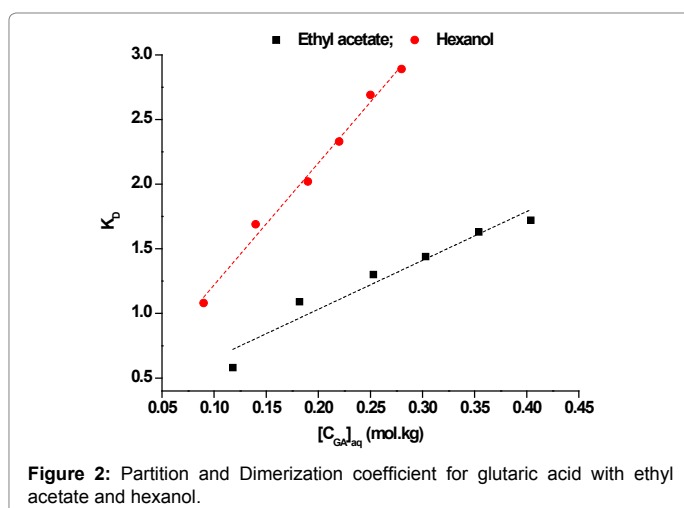


Figure 2: Partition and Dimerization coefficient for glutaric acid with ethyl acetate and hexanol.

$$\eta\% = \frac{K_D}{(1+K_D)} \times 100 \quad (4)$$

Where, [C_{GA}]_{aq} and [C_{GA}]_{org} are the total concentration of glutaric acid in aqueous and organic phase respectively. Physical extraction results were shown in Table 2. Distribution coefficients of glutaric acid with ethyl acetate and hexanol were obtained as 0.58 to 1.72 and 1.08 to 2.89 respectively. The average extraction efficiency was found to be ~ 55% in ethyl acetate and ~ 66.5% in hexanol. It can be due to hexanol is protic

diluent	$[C_{GA}]^o$	$[C_{GA}]_{aq}$	$[C_{GA}]_{org}$	K_D	η (%)	P	D	R ²
EA	1.1	0.404	0.696	1.72	63.3	0.275	25	0.93
	0.93	0.354	0.578	1.63	62			
	0.74	0.303	0.437	1.44	59.1			
	0.58	0.253	0.328	1.3	56.5			
	0.38	0.182	0.198	1.09	52.2			
	0.19	0.118	0.069	0.58	36.8			
HX	1.1	0.28	0.817	2.89	74.3	0.276	61.92	0.99
	0.93	0.25	0.679	2.69	72.9			
	0.74	0.22	0.518	2.33	70			
	0.58	0.19	0.388	2.02	66.9			
	0.38	0.14	0.239	1.69	62.8			
	0.19	0.09	0.097	1.08	51.9			

^aStandard uncertainties u are u(T)= ± 1 K, u(C_{GA})= ± 0.001 mol/kg

Table 2: Determination of partition coefficient and dimerization constant for physical extraction of glutaric acid^a.

diluent contain hydrogen atoms bound to electronegative element O (-OH) is a hydrogen bond donor and large value of relative permittivity and transmission energy indicates its strong polar nature. Thus hexanol provide high distribution coefficient values over ethyl acetate since it is good anion solvators due to their hydrogen bonding ability.

Reactive extraction of glutaric acid with tri-n-butyl phosphate

Chemical (reactive) extraction of glutaric acid and organic solution (tri-n-butyl phosphate+ diluents) can be expressed as:



The equilibrium complexation constant (K_E) can be calculated by Eq. 6.

$$K_E = \frac{[C_{GA} : C_{TBP}]_{org}}{[C_{TBP}]_{org} [C_{GA}]_{aq}} \quad (6)$$

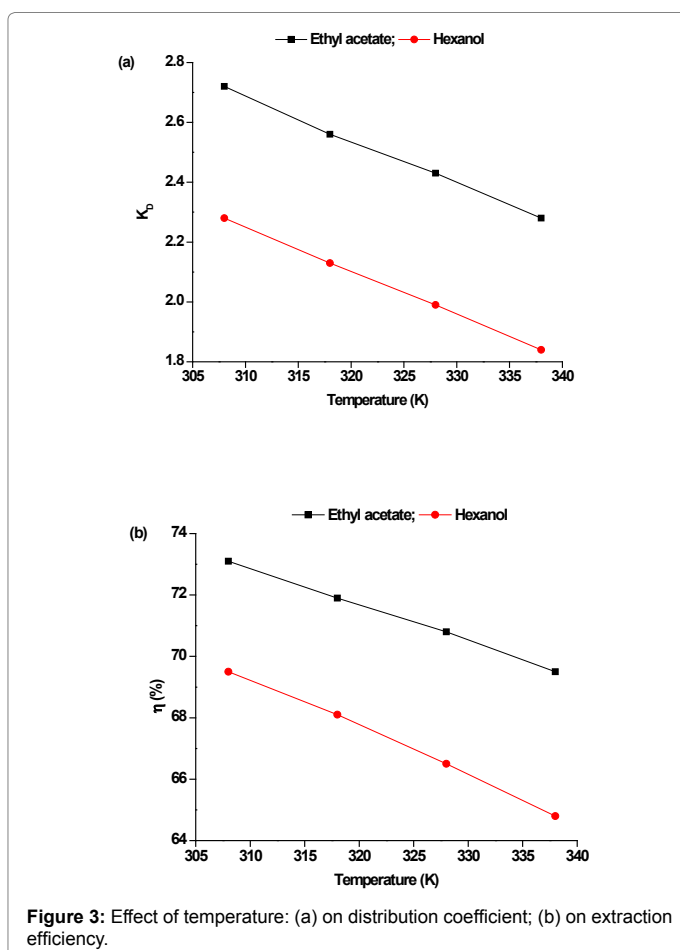
From Figure 3a, it was observed that the distribution coefficient was inversely proportional to the temperature for both diluents due to the back extraction of the acid from the organic to fresh aqueous phase. It was decrease in the range of 2.72-2.28 for ethyl acetate and 2.28-1.84 for hexanol. Moreover, Figure 3b shows that the extraction efficiency was linearly decreases from 73.1-69.5 and 69.5-64.8 for ethyl acetate and hexanol respectively in 308-338 K temperature range. At higher temperature, the rapid enhancement of ionization of acid can be suppressed the unionization of acid so the distribution of glutaric acid in organic and aqueous solution was decreased. Table 3 shows the equilibrium complexation constant in studied temperature range average K_E value was 4.70 and 3.53 (kg/mol) for ethyl acetate and hexanol respectively.

Glutaric acid – tri-n-butyl phosphate complex in diluents

The solvation number for glutaric acid – tri-n-butyl phosphate system is same as the number of carboxylic group in acid [5]. Hence, it is assumed that only 2:1 glutaric acid – tri-n-butyl phosphate complex is present in both diluents. The formation of other complexes, 1:1, 3:1 depend on concentration of the species and loading ratio. The loading ratio (ϕ) is defined as the ratio of total concentration of acid in organic solution to the initial concentration of extractant it can be expressed as:

$$\phi = \frac{[C_{GA}]_{org}}{[C_{TBP}]_{org}} \quad (7)$$

1:1 glutaric acid – TBP complex:



$$\frac{\phi}{1 - \phi} = K_E [C_{GA}] \quad \text{and } \phi < 0.5 \quad (8)$$

2:1 glutaric acid – TBP complex:

$$\frac{\phi}{2 - \phi} = K_E [C_{GA}]^2 \quad \text{and } \phi > 0.5 \quad (9)$$

3:1 glutaric acid – TBP complex:

diluent	temperature	K_D	η	K_E	ϕ	ΔG	H	ΔS	R^2
	K		%	kg/mol		kJ	J/mol	J/mol.K	
EA+TBP	308	2.72	73.1	5.34	0.652	-518.34	-935.06	-1.35	0.996
	318	2.56	71.9	4.88	0.641	-504.81			
	328	2.43	70.8	4.49	0.631	-491.28			
	338	2.28	69.5	4.1	0.62	-477.75			
HX+TBP	308	2.28	69.5	4.1	0.62	-436.17	-1110.38	-2.19	0.991
	318	2.13	68.1	3.7	0.607	-414.28			
	328	1.99	66.5	3.33	0.593	-392.39			
	338	1.84	64.8	2.98	0.578	-370.5			

^aStandard uncertainties u are u(T)= ± 1 K, u(C_{GA})= ± 0.001 mol/kg

Table 3: Effect of temperature and thermodynamic parameters of reactive extraction of glutaric acid^a.

$$\frac{\phi}{3-\phi} = K_E [C_{GA}]^3 \quad \text{and } \phi \gg 0.5 \quad (10)$$

Only 2:1 glutaric acid–tri-n-butyl phosphate complex was formed in ethyl acetate and hexanol as the dilute concentrations of glutaric acid were used in present study. The nominal difference among K_E values in both diluents for glutaric acid shows that solvation is a crucial for reactive extraction of carboxylic acid. For higher concentrations of acid in aqueous phase, 3:1 complexes may be formed. The proportions of 2:1 to 3:1 complex depend on type of diluent and its properties [6]. The loading ratio value was found to be ~ 0.6 for all cases except some points as shown in Table 3.

Effect of temperature

Heat of mixing of organic solution using distribution coefficient can be calculated by Eq. 11 [6].

$$\frac{d(\ln K_D)}{d(1/T)} = -\Delta H_{\text{transfer}} \quad (11)$$

Where, $\Delta H_{\text{transfer}}$ is the heat of transfer from aqueous to organic phase. In high temperature range, change in enthalpy (ΔH) and entropy (S) of the reaction are studied [7]. The equilibrium complexation constant is correlated with temperature, enthalpy and entropy and it can be expressed by the following equation.

$$\ln K_E = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (12)$$

Moreover Gibbs free energy (ΔG) can be calculated by the following correlation:

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

Eq. 12 reveals that, the plot (Figure 4) between $\ln(K_E)$ and $1/T$ gives straight line. The slope and intercept of straight line gives enthalpy and entropy of reaction correspondingly. Overall equilibrium constants for both the diluents were found to be decrease as the temperature increase from 308-338 K this is probably due to the back extraction of the glutaric acid. Table 3 shows the negative magnitude of both thermodynamic functions viz. enthalpy and entropy for ethyl acetate and hexanol indicates that all the reactions are exothermic reaction. ΔH and was 935.06 and 1110.38 J/mol whereas, ΔS was -1.353 and -2.189 J/mol.K for ethyl acetate and hexanol respectively. This behaviour also confirms that at higher temperatures, the reactive system becomes more unstable and hence the possibility of back-extraction increases. Decrease in ΔS reveals that, increase of the order of system due to complex formation. By the

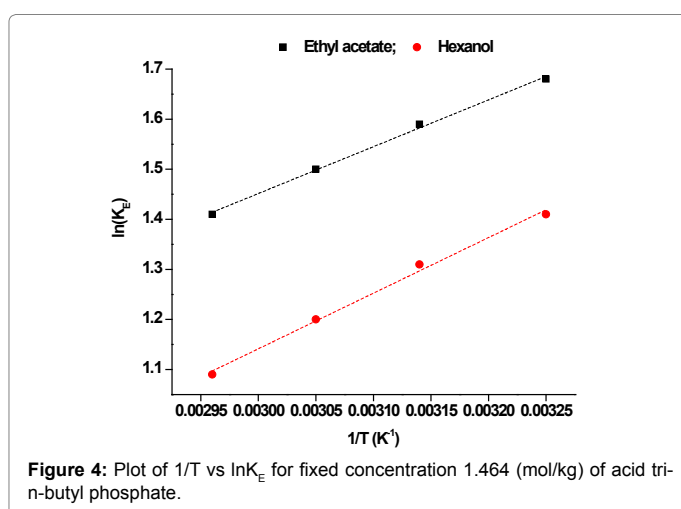


Figure 4: Plot of $1/T$ vs $\ln K_E$ for fixed concentration 1.464 (mol/kg) of acid tri-n-butyl phosphate.

formation of complexes the number of degree freedom decreases as two molecules are combined to form one entity. The results of present study were compared with reactive extraction of other carboxylic acids which is tabulated in Table 3.

The overall effect of temperature is attributed to the effects of different parameters such as pK_a , the acid-extractant interaction, solubility of the acid in both phases, the extractant basicity and water co-extraction [8]. The pK_a values of common carboxylic acids decrease slightly with an increase in temperature, leading to the dissociation of acid molecules in the aqueous phase and lower extraction efficiency. Similarly, the solubilities of acid in both aqueous and organic phases are affected by temperature. It is observed that the solubilities of carboxylic acids in water increase as the temperature increased from 278.15 to 338.15K [9].

Conclusion

Reactive extraction of glutaric acid with tri-n-butyl phosphate in ethyl acetate and hexanol was studied. P and D values for glutaric acid in ethyl acetate and hexanol were obtained as 0.275, 25.00, and 0.276, 61.92 respectively. The K_D values were found in the range of 0.58 to 1.72 for ethyl acetate and 1.08 to 2.89 for hexanol. The average extraction efficiency was found to be ~ 55% in ethyl acetate and ~ 66.5% in hexanol. The loading ratio value was found to be ~0.6 for all cases i.e., it is assumed that only 2:1 glutaric acid–tri-n-butyl phosphate complex is present in both diluents. Thermodynamic function enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) were calculated as negative magnitude of enthalpy confirms the glutaric acid extraction with both diluents is exothermic reaction. Increasing values of temperature are

inversely proportional to the distribution coefficient and extraction efficiency. This behavior also confirms that at higher temperatures, the reactive system becomes more unstable and hence the possibility of back-extraction increases.

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