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Gallic acid extraction with mixed aminic extractants dissolved in 1-decanol

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Gallic acid (GA) is a one of those phenolic acids which has a significant role in different industrial applications. In present study, the organic phase volume of TOA-Aliquat336 extractant mixture dissolved in 1-decanol is optimized for the maximum recovery of GA by synergic extraction. The effects of acid concentration, extractant volume ratio, solvent polarity and pH of initial aqueous solution on GA extraction, are examined. The 1:1 acid-extractant complexation is considered as the acid loading ratio *Z* and the number of reacting acid molecules per molecule of extractant *m*, are found <0.5 and 1.11 respectively. With the effect of synergism, the maximum extraction is found 98.37% with 10% TOA-20% Aliquat336 extractant mixture dissolved in 70% 1-decanol for initial gallic acid concentration of 0.02939 kmol.m^{-3}. For the extraction yield >95%, the optimum organic phase volume of 10% TOA-5% Aliquat336 in 85% of 1-decanol is selected for the synergic extraction of GA.

Keywords: Gallic Acid, Tri-n-octylamine, Tricaprylmethylammonium chloride, Synergic extraction, Distribution coefficient

Introduction

Gallic acid (GA) is a trihydroxybenzoic acid with both acidic (-COOH) and alcoholic (-OH) functionality (pKa_{COOH} = 4.4 and pKa_{OH}= 9.98)[1]. With the family of the natural phenolic acids, it is distributed in various plant leaves, pulp, roots, fruit shell etc.[2]. The molecular structure of GA is shown in Fig. 1. With the anti-oxidant, anti-fungal, anti-inflammatory, anti-viral medicinal abilities, it is used as a drug molecule GA. It is a key ingredient in manufacturing of different category medicines (anti-cancer, antiviral, antibiotic etc.). It is a key molecule in lauryl gallate, propyl gallate and dodecyl gallate, which are used as food preservatives[3]. The tannin hydrolysis process is main source of GA production but economically non-viable. Nowadays, the microbial fermentation pathways are the alternate source of GA producton[4]. Therefore, with the economic perspectives, the researchers are going on for the recovery of GA from its different sources of aqueous streams.

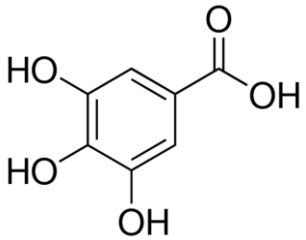

Fig. 1. Molecular structure of gallic acid

Among different recovery methods, such as adsorption[5], biofiltration[6], precipitation[7], ultrafiltration[8], the reactive solvent extraction also known as reactive

extraction is found environment friendly, energy saving and cost-effective method by many researchers for the various organic acid's recovery from the aqueous streams[9]. In reactive extraction process, the solute recovery from its aqueous solution is done by an organic solution. In this organic solution the extractant such as aliphatic amine with high molecular weight is dissolved in other organic diluents such as ketone, alcohol and other hydrocarbons for better solvation. On the mixing of aqueous and organic phases the solute is distributed in both the phases and formed a complex with extractant molecule. The formation of solute-extractant complexes depends on the nature of the diluent, temperature, pH of initial aqueous phase etc.[10,11]. The researchers have also approached for synergic extraction of different organic acids with aminic and phosphoric extractants[12-14]. In the synergic extraction process, two or more extractants are mixed in organic phase with diluent for the extraction of a solute from the aqueous phase. It is called a positive synergism when the extraction efficiency of mixture of extractants is higher to the sum of the efficiencies of each individual extractant and vice-versa[15]. Positive synergism is appeared when the hydrophobicity of the extracted complex is improved by solvation and it is done by addition of extractants with high polarity difference[14].

Theoretical Modelling

The assumptions for the reactive extraction process are, (i) the miscibility of extractant and diluents in water is negligible, (ii) No water coextraction with acid is there, (iii) and

At equilibrium, there is no volume change in both the phases.

The dissociation of Gallic acid (GA) occurs in the aqueous phase, at equilibrium (Eq. 1).

$$HG \xleftrightarrow{K_a} H^+ + G^- \qquad (1)$$

The dissociation constant (K_a) is calculated by Eq. 2.

$$K_a = \frac{[H^+][G^-]}{[HG]} \qquad (2)$$

The combined concentration of dissociated ($[G^-]$) and un-dissociated ($[HG]$) acid, expresses the total concentration of GA in the aqueous phase (C_{HG}), as given in Eq. 3.

$$C_{HG} = [HG] + [G^-] = [HG]\left(1 + \frac{K_a}{[H^+]}\right) \qquad (3)$$

It is assumed that *m* un-dissociated acid (HG) molecules are reacting with *n* extractant molecules to form the acid-extractant complex in an interfacial reaction (Eq. 4).

$$mHG + n\overline{A} \xleftrightarrow{K_E} \overline{(HG)_m(A)_n} \qquad (4)$$

$$K_E = \frac{\overline{(HG)_m(A)_n}}{[HG]^m + [\overline{A}]^n} \qquad (5)$$

where, K_E is the equilibrium constant for acid-extractant complexation reaction.

The distribution coefficient (K_D) is defined as the ratio of organic phase GA composition ($\overline{C}_{HG}$) to aqueous phase GA composition (C_{HG}) at equilibria (Eq. 6).

$$K_D = \frac{\overline{C}_{HG}}{C_{HG}} = m\frac{\overline{[(HG)_m(A)_n]}}{C_{HG}} \qquad (6)$$

Putting the values from Eq. 3, Eq. 4 and Eq. 5, another equation (Eq. 7) can be rearranged for the distribution coefficient (K_D),

$$K_D = \frac{mK_E C_{HG}^{m-1}[\overline{A}]^n}{\left(1 + \frac{K_a}{[H^+]}\right)^m} \qquad (7)$$

Eq. 8 represents the extractant concentration remained free in organic solution ($[\overline{A}]$) at equilibria after the reaction.

$$[\overline{A}] = \overline{C}_{A,o} - n\overline{[(HG)_m(A)_n]} \quad (8)$$

Where, $\overline{C}_{A,o}$ is the total initial extractant concentration in the organic phase.

Putting the values from Eq. 6 and Eq. 9, the Eq. 8 can be rearranged for $[\overline{A}]$ as,

$$[\overline{A}] = \overline{C}_{A,o} - K_D \frac{nC_{HG}}{m} \quad (9)$$

Putting the value of $[\overline{A}]$ from Eq. 9 to Eq. 7, the Eq. 10 is found for K_D values.

$$K_D = mK_E \left(\overline{C}_{A,o} - K_D \frac{nC_{HG}}{m}\right)^n \frac{C_{HG}^{m-1}}{\left(1+\frac{K_a}{[H^+]}\right)^m} \quad (10)$$

The numerical method is employed on Eq. 10 to calculate the K_E and stoichiometric coefficients, *m* and *n*. A statistical function as expressed by Eq. 11 is used to minimize the error between the experimental and model predicted K_D values.

$$rmsd = \sqrt{\frac{\sum_1^N (K_{D,exp} - K_{D,pred})^2}{N-1}} \quad (11)$$

where, N is the total number of experimental data points.

Loading ratio, Z, i.e. the acid loading in organic phase, is calculated by Eq. 12.

$$Z = \frac{\overline{C}_{HG}}{\overline{C}_{A,o}} \quad (12)$$

The value of Z < 0.5 indicates the acid:extractant (1:1)complex formation in organic phase[12].

In present study, the equilibrium studies for synergic extraction of gallic acid with the optimized organic phase mixture of TOA-Aliquat336-decanol are carried out. The extraction yield along with reaction stoichiometry is discussed.

Materials and Method

Two extractants: (i) tri-n-octylamine, TOA (Molar mass: 353.67 g.mol^{-1} and density: 0.809 g.cm^{-3}) and Tricaprylmethyl ammonium chloride, Aliquat 336 (Molar mass: 404.16 g.mol^{-1} and density: 0.884 g.cm^{-3}) were supplied by Spectrochem. Pvt. Ltd., India, with assay of > 98%. 1-Decanol as a polar diluent/modifier [specific gravity = 0.829 g.cm^{-3} with > 98% assay] was supplied by Spectrochem Pvt. Ltd., India. Gallic acid, GA (Molar mass: 170.12 g.mol^{-1} and density: 1.694 g.cm^{-3}), a pale fawn-colored crystals, was procured from Sigma-Aldrich USA with >98% assay. No further purification of chemicals has done, they were used as they imported.

The stock solution (0.04703 kmol.m^{-3}) of GA was used to prepare the aqueous samples of different concentration by serial dilution in Milli-Q water at 298.15±1K. The required organic solutions were prepared by mixing different volume ratio of TOA and Aliquat-336 in 1-decanol. Equal volumes (20-20 ml) of aqueous and organic phase were taken in the conical flasks (100 ml, screw capped) and agitated in the temperature controlled shaking bath (Make: M/s Labtech and model: LSB-0305) at 150 rpm. After 6 hours agitation the equilibrium was achieved and the samples were transferred to separating funnel (60 ml) for phase separation. After 2 hours the organic and aqueous phase were clearly separated due to their density difference. Now, the separated aqueous samples were analyzed using UV spectrophotometer (Make: Motras Scientific, India; Model: UV PLUS) at wavelength, λ_{max} = 261 nm. Using material balance the GA

concentrations of organic phase were calculated. The experiments were performed twice in numbers and the result reproducibility was found within ±5% of error. The calculation of extraction yield in terms of percent extraction efficiency (*E*) was done by Eq. (13).

$$E = \frac{\overline{C}_{HG}}{C_{HG,o}} \times 100 \qquad (13)$$

Where, $C_{HG,o}$ represents initial concentration of GA in aqueous phase.

Results and Discussion

Organic Phase Optimization

Taking into account of previous works on synergic extraction of researchers[9-23], for the optimization of the organic phase volume, TOA concentrations 0.22874 (10% v/v) and 0.45749 (20% v/v) kmol.m^{-3} are selected with varying concentrations of Aliquat 336 (0% - 30% v/v organic phase) for extraction of a fixed initial GA concentration 0.02939 kmol.m^{-3}. 1-Decanol, as a polar diluent has been proven for providing better solvation for the extraction of organic acids[12]. The distribution coefficient (K_D) and degree of extraction (*E*) are calculated to analyze the best suitable organic phase volume for synergic extraction of GA (Table 1).

As shown in Fig. 2, the degree of extraction of GA dramatically jumps to > 95% with just an addition of 5% (v/v) Aliquat336 with 10% or 20% TOA. The maximum extraction is found 98.37% at 10% TOA and 20% Aliquat336 extractant mixture dissolved in 70% 1-decanol. Aliquat336 has a high viscosity (1.5 × 10^6 cP at 303.15 K) and therefore, higher concentration of Aliquat336 can cause a third phase formation while extraction of GA. Thus, with optimization point of view, 10% TOA with 5% Aliquat336 dissolved in 1-decanol is chosen for the synergic extraction of GA. The GA extraction yield greater than 97% is found at this optimized condition.

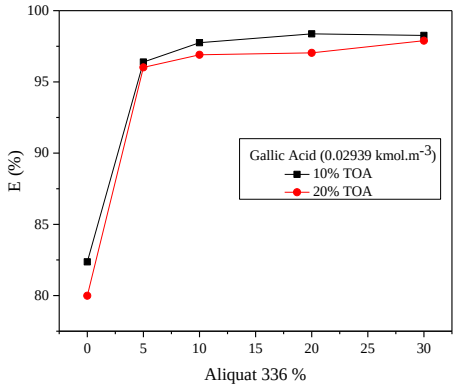

Fig. 2. Organic phase optimization for synergistic extraction

The TOA concentration 0.22874 kmol.m^{-3} (10% v/v) and Aliquat336 concentration 0.10936 kmol.m^{-3} (5% v/v) are mixed in 1-decanol for the synergic extraction of different initial GA concentrations (0.00294, 0.01176, 0.02351, 0.03527 and 0.04703 kmol.m^{-3}) at 298.15±1 K. The equilibrium results are shown in Table 2.

The isotherm for acid distribution in aqueous and organic phase is shown in Fig. 3.

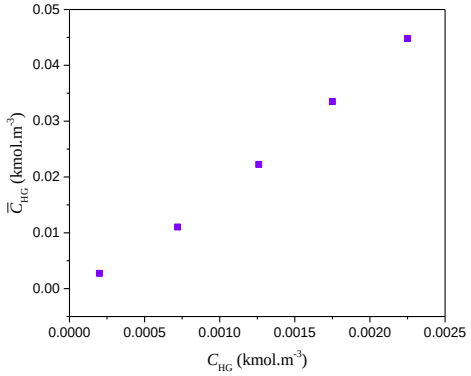

Fig. 3. Isotherm for distribution of GA in aqueous and organic phase at 298.15±1 K.

Table 1. Organic phase optimization for $C_{HG,o}$ = 0.02939 kmol.m^{-3}.

TOA Conc. (kmol m^{-3})	Aliquat 336 (% v/v)	Aliquat 336 Conc. (kmol m^{-3})	C_{HG} (kmol m^{-3})	$\overline{C}_{HG}$ (kmol m^{-3})	K_D	E (%)
0.22874 (10% v/v)	0	0	0.00518	0.02421	4.67	82.37
	5	0.10936	0.00106	0.02833	26.73	96.39
	10	0.21873	0.00066	0.02873	43.53	97.75
	20	0.43745	0.00048	0.02891	60.23	98.37
	30	0.65618	0.00051	0.02888	56.63	98.26
0.45749 (20% v/v)	0	0	0.00588	0.02351	4	79.99
	5	0.10936	0.00117	0.02822	24.12	96.02
	10	0.21873	0.00091	0.02848	31.3	96.9
	20	0.43745	0.00087	0.02852	32.78	97.04
	30	0.65618	0.00062	0.02877	46.4	97.89

Table 2. Equilibrium synergic extraction results of GA from aqueous solution using 10%TOA-5%Aliquat336 in 85% Decanol at 298.15 ± 1 K.

$C_{HG,o}$ (kmol m^{-3})	C_{HG} (kmol m^{-3})	$\overline{C}_{HG}$ (kmol m^{-3})	K_D	$K_{D,Avg}$	E (%)	E_{Avg} (%)	Z	pH	m	K_E
0.00294	0.0002	0.00274	13.7	17.15	93.2	94.4	0.0081	4.05	1.11	127.68
0.01176	0.00072	0.01104	15.33		93.88		0.03265	3.77		
0.02351	0.00126	0.02225	17.66		94.64		0.06581	3.65		
0.03527	0.00175	0.03352	19.15		95.04		0.09914	3.58		
0.04703	0.00225	0.04478	19.9		95.22		0.13245	3.52		

The distribution coefficient obtained experimentally is compared with model (Eq. 10) predicted distribution coefficient in Fig. 4.

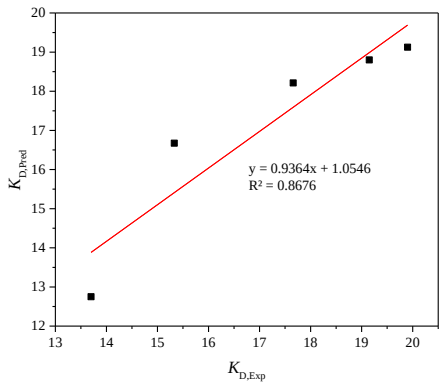

Fig. 4. $K_{D,Exp}$ versus $K_{D,Pred}$ graph.

The average distribution coefficient ($K_{D,Avg}$) and extraction yield (E_{Avg}) is obtained 17.15 and 94.14% respectively. The acid loading ratio (Z) is found in range of 0.008 – 0.132, indicates the 1:1 acid-extractant complexation in the organic phase. The GA molecules m reacting per molecule of extractant is found 1.11 and the value of reaction equilibrium constant K_E is calculated 127.68.

Conclusions

Considering the extraction yield ≥95%, the TOA concentrations 0.22874 kmol.m^{-3} with Aliquat336 concentration 0.10936 kmol.m^{-3} dissolved in 1-decanol is found a favorable organic phase for the extraction of GA from aqueous solutions. The Z values and m indicate the 1:1 complex formation between extractant (TOA and Aliuqat 333) and gallic acid.

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