



Extraction of levulinic acid using tri-*n*-butyl phosphate and tri-*n*-octylamine in 1-octanol: Column design



Dipaloy Datta^a, Mustafa Esen Marti^b, Hasan Uslu^{c,d}, Sushil Kumar^{e,*}

^a Malaviya National Institute of Technology (MNIT), Department of Chemical Engineering, Jaipur, Rajasthan, India

^b Department of Chemical Engineering, Selcuk University, Konya, Turkey

^c Beykent University, Engineering and Architecture Faculty, Chemical Engineering Department, Ayazağa, İstanbul, Turkey

^d Chemical and Materials Engineering Department, Faculty of Engineering, King Abdulaziz University, Jeddah, Saudi Arabia

^e Department of Chemical Engineering, Motilal Nehru National Institute of Technology (MNNIT), Allahabad, Uttar Pradesh, India

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ABSTRACT

The reactive extraction of levulinic acid using two different extractants [tri-*n*-butyl phosphate (TBP) and tri-*n*-octylamine (TOA)] dissolved in 1-octanol was investigated at 298 K. Using the equilibrium data, the distribution coefficient (K_D), extraction efficiency (%*E*) and loading ratios (*Z*) were calculated. TOA provided highest K_D values with 1-octanol. A maximum K_D was obtained as 9.571 using 0.689 mol/kg TOA while 90.54 % of the initial levulinic acid was extracted. Increasing the initial acid concentration resulted in a decrease in the extraction efficiency. Loading ratios were found to be less than 1 for TBP while both types, i.e. 1:1 and 2:1 acid-amine complexes were expected to form with TOA. The feasibility of the extraction process was assessed by calculating minimum solvent to feed ratio required for 90% recovery of levulinic acid, number of theoretical stages, height and diameter of the extraction column.

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1. Introduction

Liquid–liquid extraction is a separation technique to isolate and concentrate valuable components from an aqueous solution by using an organic solvent. Extraction is often applied when other separation techniques like distillation, adsorption, electrodialysis, membrane separation, etc. are ineffective and inefficient. Nowadays, extraction finds its application in separation, purification or enrichment of the product in the mining industries, environmental applications, recovery of organic and inorganic acids, organic chemistry intermediates and pharmaceuticals [1]. The reactive extraction has potential to recover organic acids from their dilute aqueous medium or fermentation broth [2–5]. The method has been known for the advantages like (i) effective at high concentration of substrate in the extractive fermentation, (ii) easy re-extraction of acid and reuse of solvent, (iii) improved pH control in bio-reactor, (iv) better recovery of acid with high product purity, (v) decrease in downstream processing load and recovery cost, and (vi) phase equilibrium enhanced [5–9]. In the reactive extraction, the extractant molecule reacts with the solute molecule, and thus

solvates the formed complex in the organic phase which makes it different from traditional extraction process. Long chain aliphatic amines (tri-*n*-octyl amine, tri dodecyl amine, etc.) and organophosphorous solvents (tributylphosphate, trioctylphosphine oxide, etc.) are proposed as appropriate extractants for the reactive extraction [10]. These extractants are generally used with diluents which have significant effect on the extent of extraction. Non-aromatic, water immiscible and polar solvents with intermediate molecular weights and high boiling points are commonly preferred for the extraction to have high distribution and selectivity [11].

Levulinic acid ($H_8C_5O_3$), or gamma-ketovaleric acid, a short chain fatty acid, has a ketone carbonyl group (CO) and an acidic carboxyl group (COOH). It is a versatile chemical with numerous potential uses, and has received considerable attention due to its potential use as an important basic chemical. Kitano et al. (1975) and Ghorpade and Hanna (1999) reviewed the properties of levulinic acid, and suggested potential uses as polymer resin, plasticizer, textile dye, animal feed additive, fuel extender, antifreeze and food antimicrobial agent [12,13]. Traditionally, levulinic acid is synthesized via the controlled degradation of hexose sugars by mineral acids. Raw materials used for levulinic acid production included simple sugars, starch and cellulosic materials.

The first synthesis of levulinic acid by heating sucrose with mineral acids at high temperature was reported in the 1840s by the Dutch professor Mulder [14]. This versatile renewable

* Corresponding author.

E-mail addresses: dipaloy@gmail.com (D. Datta), marti@selcuk.edu.tr (M.E. Marti), hasanuslu@gmail.com (H. Uslu), sushilk2006@gmail.com, drsushilk2010@gmail.com (S. Kumar).

platform molecule has also been identified by the US Department of Energy as one of the 12 top value-added biochemicals [13]. Levulinic acid is a commodity chemical that finds applications for several purposes, such as source of polymer resins, animal feed, food as well as components of flavoring and fragrance industry, textile dyes, additives, extenders for fuels, antifreeze products, antimicrobial agents, herbicides and also plasticizers [16,17]. Traditionally, the most convenient industrial route to levulinic acid involves production from hexose sugars [17]. More recently, the utilization of biomass and agricultural wastes for production of levulinic acid has been subject to increased interest as a research topic, since it would render the process cheaper due to the high availability and low cost of raw materials. Levulinic acid demand for agriculture applications or other pesticides, and for pharmaceutical applications is expected to grow at a Compound Annual Growth Rate of 6% and 5.4%, respectively, from 2014 to 2020. The market volume share by application in 2013 of this acid is 23.2% for pharmaceuticals, 42.8% for agriculture, 21% for food additive, and 13% for cosmetics [6,18,19].

The survey of the literature showed that the study on the reactive extraction of levulinic acid is limited reported, so far. Fan and Yan [20] studied degradation of cellulose to levulinic by liquefaction of biomass at high pressure in a continuous extraction method using 1,2-dichloroethane as a solvent, and obtained a maximum yield of 30.66% of the acid. Uslu and his co-workers reported the reactive extraction of levulinic acid using Amberlite LA-2 (0.371–1.859 mol/L) [21] + (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate, isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, diisobutyl ketone and methyl isobutyl ketone), trioctylamine (0.590–1.731 mol/L) [22] + (ethyl propionate, dimethyl phthalate, hexyl acetate, cyclohexyl acetate, dimethyl adipate, propyl acetate, dimethyl glutarate, dimethyl fumarate, diethyl sebacate, and diethyl carbonate), tripropyl amine [23] + toluene, and Aliquat 336 (0.464–1.692 mol/dm³) [24] + (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate, diisobutyl ketone, and methyl isobutyl ketone). Kumar et al. [5] presented extraction equilibrium results of levulinic acid using trioctylamine (0.573 kmol/m³) dissolved in decane, decan-1-ol, decane + decan-1-ol (1:1 v/v), toluene, methyl isobutyl ketone, and dichloromethane. An extraction efficiency of 98.7% was reported with trioctylamine + dichloromethane system. Şenol [25] focused on the partitioning of formic and levulinic acids between aqueous and organic phases using Alamine 308 or triisooctylamine (0.02–0.11 kmol/m³) as extractant, and cyclohexanone, methylcyclohexanol, 1,2-dichlorobenzene, and toluene. The author reported that cyclic alcohol + amine system yielded the highest synergistic extraction efficiency among the different systems used. In another study by Şenol [26], the extractability of formic, levulinic and acetic acids from their single acid solutions was investigated using Alamine 336 dissolved in different diluents. The results were correlated using a modified linear solvation energy relation, mass action law, and a modified version of the Langmuir equilibrium model. Uslu et al. [27] determined the liquid–liquid equilibria (LLE) for water + levulinic acid + dibasic esters ternary systems. The LLE data were correlated with UNiVersal QUAsiChemical (UNIQUAC) and Non-random two-liquid (NRTL) models.

The objective of the present study is to analyze the effect of two extractants namely a phosphorus bonded oxygen donor extractant, tri-*n*-butyl phosphate and an amine based extractant, tri-*n*-octylamine on the recovery of levulinic acid by reactive extraction from dilute aqueous solutions. According to earlier findings, alcohols are the most efficient diluents used in the extraction due to their best solvation property for the acid-extractant complexes formed [7,28]. Solvent polarity is one of the most important char-

acteristics in solvating an acid-extractant complex during the extraction. Normally, the polar nature of solvent decrease with an increase in the number of carbon present in it. The polarity of first three alcohols namely methanol, ethanol and propanol is more due to the strength of –OH group, and hence completely soluble in water in any proportion. With an increase in the carbon number, the solubility of alcohols decreases. Therefore, 1-octanol with intermediate carbon number was chosen in the current study.

2. Materials and methods

The chemicals used are listed in Table 1 with their physical properties. The levulinic acid concentration in the aqueous solution was found to be less than 10% w/w [23], and therefore initial concentration of acid was considered from 0.111 to 0.541 mol/kg. The organic solvent phase was prepared by dissolving TBP (0.365–2.192 mol/kg), and TOA (0.115–0.689 mol/kg) in 1-octanol. 20 mL of each phase was taken in the conical flask of 100 mL, and shaken at 100 rpm for 6 h in a temperature controlled reciprocating water shaker bath (HS 250 basic REMI Labs, India) at a constant temperature of 298 K. After attaining equilibrium, the mixture was kept in a separating funnel (60 mL) for 2 h at 298 K for clear separation of phases. Now, the aqueous solution was analyzed to determine the concentration of levulinic acid at equilibrium with titration using fresh NaOH solution of 0.01 N, and phenolphthalein as an indicator. The acid concentration in the organic phase was calculated by mass balance. The organic solvents like TBP, TOA, and 1-octanol are almost insoluble in water. Also, water co-extraction in the organic phase by the solvents is less [29]. Therefore, the change in the volume of each phase was neglected in the calculation of distribution coefficient, degree of extraction and loading ratio.

3. Theory

The active solvent, 1-octanol, and the extractants (tri-*n*-butyl phosphate and tri-*n*-octylamine) used in this study are poorly soluble in water. The solubility of alcohols in water depends on the number of carbon atoms present in them (methanol, ethanol and propanol are completely soluble in water but solubility decreases with increase in carbon number like 1-octanol, 1-decanol). Also, the solvent phase co-extract water in lesser amounts with carboxylic acids [30,31]. Therefore, distribution coefficients and other parameters are calculated by assuming negligible solubility of solvents in the aqueous phase. The separation of levulinic acid, a mono-carboxylic acid, by the extractants dissolved in an intermediate molecular weight alcohol can be presented by an interfacial reaction taking place between *m* molecules of acid (HA) and one molecule of extractant (T) to form various (*m*:1) acid-extractant complexes (Eq. (1)) with apparent equilibrium constant (K_E) (Eq. (2)).



With an expression of equilibrium constant as follows:

$$K_E = \frac{\bar{C}_{m1}}{[\text{HA}]^m [\bar{T}]} \quad (2)$$

The distribution coefficient (K_D) can be determined by Eq. (3).

$$K_D = \frac{\bar{C}_{\text{HA}}}{C_{\text{HA}}} \quad (3)$$

where \bar{C}_{HA} and C_{HA} are the total levulinic acid concentration in the organic and aqueous phase, respectively.

The total amount of acid present in the organic phase (\bar{C}_{HA}) will be extracted by the extractant (in chemical extraction, $m\bar{C}_{m1}$), and

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