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Liquid-liquid equilibria for (volatile fatty acids + water + alcohol ethoxylates): Experimental measurement of pseudo-ternary systems

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ABSTRACT

Experiments were conducted to establish the phase diagrams for ternary systems containing (acetic acid or propionic acid or butyric acid + water + alcohol ethoxylate surfactant) at 308.15 K and ambient pressure. Results indicated that the systems belong to Type 1 Treybal classification with water–surfactant binary pair exhibiting partial miscibility. The liquid–liquid equilibrium data were used to determine the ability of the surfactant to extract the acids from aqueous solutions. The calculated distribution coefficients and separation factors indicated that the effectiveness of the surfactant to extract acids follow the trend: butyric acid > propionic acid > acetic acid. The effectiveness of the surfactant to extract butyric acid from aqueous solutions is similar to previously studied environmentally-friendly solvents with added benefit of being non-inhibitory to microbial growth and metabolism. These characteristics of the alcohol ethoxylate used in this study could be exploited for the development of an extractive butyric acid fermentation process.

1. Introduction

In the United States, more than 226 × 10^6 tonnes of municipal solid wastes (MSW) and ~ 47.7 × 1012 L of municipal wastewater are generated annually [1,2]. With strict regulatory requirements on disposal as well as heightened environmental concerns, sustainable treatment of these urban wastes has become a goal of technical explorations and experimentations. Instead of waste streams to be treated and disposed of, these urban wastes are considered to be resources that can be processed for the recovery of materials, energy, and nutrients [3]. Through the Food-Energy-Water (FEW) Nexus, these urban wastes have become a major research initiative across the globe through several international agreements and governmental policies [4,5,6,7]. In particular, the utilization of these wastes is of great interest because of the potential to convert urban areas (cities) into future sources of food (animal feed), energy (fuels), water (reclaimed) and chemicals production [8,9] (Fig 1).

One group of chemicals that can be obtained from urban waste streams are short chain fatty acids, also known as volatile fatty acids (VFAs). Presently, these VFAs (*e.g.* acetic, propionic, butyric acids) are primarily produced today via chemical synthesis using petrochemical feedstocks [10]. VFAs in the C_1–C_4 range are important commodity chemicals with wide range of applications in the food, pharmaceutical, polymer and biofuel industries [11,12]. In addition to being a food additive, acetic acid (C_2) also serves as raw material for the production of polyethylene terephthalate (soft drink bottles), cellulose acetate (photographic film), polyvinyl acetate (wood glue), and synthetic fibres and fabrics. Propionic acid (C_3) is used in the synthesis of cellulose fibres (cellulose acetate propionate), herbicides, perfumes, food and grain preservatives, and pharmaceuticals [11]. Lastly, butyric acid (C_4) is being used to produce thermoplastics (*e.g.* cellulose acetate butyrate), and its esters have considerable commercial importance in the chemical, textile, plastic, food, beverage, dairy, and pharmaceutical industries as solvent, diluent, drug additive (anesthetics), plasticizer, perfume, fibre, additive, and raw material [12,13]. Among these applications, it is anticipated that the food industry (animal feed market in particular) will be the fastest-growing end-user of these VFAs due to increasing human population [14].

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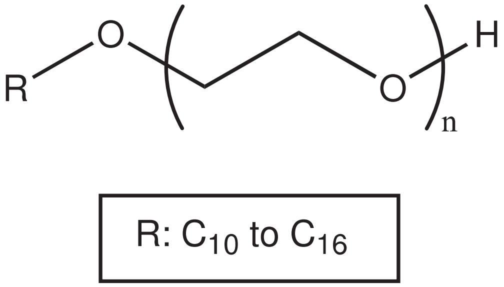

Fig. 1. The structure of C_{10}–C_{16} alcohol ethoxylates.

VFAs can be sustainably produced using urban waste streams through a biochemical process called anaerobic digestion [15]. For the case of butyric acid, their production through this route produces “renewable butyric acid” and is preferred for use in the food, flavor and pharmaceutical sectors [14]. However, this biochemical or fermentative production route is not very attractive due to challenges on downstream processes particularly the separation of the acid from the aqueous mixture [16,17]. In addition, large-scale fermentative production of VFAs is hindered by low product concentration and productivity due to product inhibition. That is, high VFAs concentration inhibits microbial activities, which is believed to be due to pH decrease [18]. One strategy that could overcome these hindrances is *in situ* extraction or extractive fermentation. This is also known as biphasic, two-phase or phase-partitioning fermentation where generation and extraction of metabolites (in this case VFAs) are combined in a single step and could result to an 8-fold increase in process productivity [19]. Among the solvents studied for extractive fermentation of VFAs include long-chain aliphatic amines and fatty alcohols (or their mixture) due to their high distribution coefficients [19–23]. Despite tremendous previous efforts on extractive fermentation for VFAs production, the success of this strategy is hampered by solvent toxicity (to fermentation microbes) and biodegradability. Most of the solvents or solvent mixture tested for extractive VFAs fermentation are toxic to acid-forming microbes [24].

Non-ionic surfactants, particularly those that belong to the alcohol ethoxylate group offer a unique characteristic of being non-toxic to microorganisms [25–27]. In addition, their hydrophilicity/hydrophobicity or water miscibility can easily be modified by changing the length of their alcohol component as well as the number of ethoxylate units in their molecule [28]. However, phase equilibrium data are not currently available for systems containing VFAs, water, and non-ionic surfactant. Thus, this study was conducted to establish ternary phase diagrams for such systems at 308.15 K, the commonly used temperature for VFAs fermentation. Particularly, acetic, propionic and butyric acids were used as VFAs while a commercially available non-ionic surfactant (chosen based on water immiscibility) was used in this study. The surfactant is a mixture that contains C_{10}–C_{16} alcohols with 2 ethoxylate units, thus, this study technically dealt with pseudo-ternary systems. This study will serve as the theoretical foundation of the targeted *in-situ*, extractive VFAs fermentation using non-ionic surfactants.

2. Experimental

2.1. Materials

The non-ionic surfactant [Novel® 23E2 Ethoxylate (N23E2)] was provided by Sasol North America (Westlake, LA). The VFAs (acetic, propionic and butyric) were purchased from Sigma-Aldrich (St. Louis, MO, USA) while Optima® LC/MS grade water was obtained from Fisher Scientific (Pittsburgh, PA, USA). All chemicals were used as received. Table 1 shows sources, purities and some properties of these materials.

2.2. Equilibrium sample preparation and procedure

Mixtures of VFA (acetic, propionic or butyric acid), water, and N23E2 were prepared with a total weight of about 5 g. The mixtures were vortex-mixed (pulse-mode) at 3000 rpm for 1 min and were then equilibrated for at least a month (pre-determined) at 308.15 K in a Fisher Scientific low temperature incubator (Pittsburgh, PA, USA). Samples were then taken from the phases formed and were analysed for VFA, surfactant, and water.

2.3. Sample analyses

The N23E2 and VFAs were analysed using an Agilent HP1100 LC system (Agilent, Santa Clara, CA, USA) equipped with a diode array detector (DAD) and coupled to a SofTA Model 300S evaporative light scattering detector (ELSD) (Teledyne Isco, Lincoln, NE, USA). The acids were analysed using the DAD at 210 nm while the surfactants were detected on the ELSD using a mobile phase containing 80/20 (vol.) acetonitrile/water at a flowrate of 0.40 mL•min^{-1} for 1.50 min. No column was used for the analysis, only a piece of HPLC tubing (0.005″ ID x 83.5″ length) connects the injector to the detectors. The ELSD was running at a drift tube and spray chamber temperatures of 65 °C and 20 °C, respectively, throughout the duration of the analysis. (Please see the Supplementary Materials for additional information).

Analysis of the water was done using a Varian Star 3600Cx gas chromatograph (GC) equipped with a Varian 8200Cx autosampler and a Saturn 3 mass spectrometer (MS) (Varian Inc., Palo Alto, CA, USA). Helium was the carrier gas using a DB-624 column with a dimension of 30 m × 0.25 mm and with 1.4 µm film thickness. Samples were diluted with methanol prior to analysis which was conducted with an injection volume of 0.5 µL. The autosampler was programmed with a wash (methanol) time of 40 secs, uptake speed of 5.0 µL•s^{-1} and an injection rate of 10.0 µL•s^{-1}. The injector 100:1 split ratio) was set at 120 °C and the gas chromatograph oven was run isothermally at 104 °C for 3 mins. The mass spectrometer was set to scan from 15 to 24 *m/z* for the duration of the analysis.

Table 1
Materials used in this study.

Chemical Name	IUPAC Name	CAS No.	Source	Mass Fraction[a]
NOVEL® 23E2 Ethoxylate	Alcohols, C_{10-16}, ethoxylated [$RO(CH_2CH_2O)_2H$]	68002-97-1	Sasol	>0.99[b]
Acetic Acid	Ethanoic Acid	64-19-7	Sigma Aldrich	0.997
Propionic acid	Propanoic Acid	79-09-4	Sigma Aldrich	0.995
Butyric acid	Butanoic Acid	107-92-6	Sigma Aldrich	0.99
Water	Oxidane, Water	7732-18-5	Fisher Scientific	1.0

[a] Supplier provided properties.

[b] The trade name could contain up to 18% (wt.) free alcohol. The purity of the sample used in this study was determined by GC/MS (see Supplementary Materials).