Phase separation in a salting-out extraction system of ethanol–ammonium sulfate

Hongxin Fu [a,b], Shang-Tian Yang [b], Zhilong Xiu [a,*]

[a] School of Life Science and Biotechnology, Dalian University of Technology, Dalian 116024, China
[b] Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH 43210, USA

ABSTRACT

The effects of tie line length, phase volume ratio, phase continuity, degree of mixing and equipment geometry size on the kinetics of phase separation in the ethanol–ammonium sulfate salting-out extraction system were studied with tie line lengths of 42.5%, 51.4% and 56.6% and phase volume ratio in the range of 1:9–9:1. The time for product distribution and phase equilibrium was also investigated. It was found that the rate of phase separation increased as the tie line length increased and the shortest separation time was obtained at the phase inversion point for all the tie lines at a constant phase volume ratio. The phase continuity was determined not only by the phase volume ratio, but also by the degree of mixing. An ambiguity area where gentle vortex produced a top-continuous system and intense mixing produced a bottom-continuous system was observed and its scope was extended as the mixing intensity decreased. Additionally, increasing the cross-sectional area of equipment had a significant effect on the rate of phase separation because the coalescence process determined the separation rate in the salting-out extraction system. By comparing the concentration of target product (butanol) and phase-forming component (ethanol) in the top phase at different time intervals, it was concluded that this system can achieve complete phase equilibrium within 10 min. The knowledge of kinetics of phase separation is important to the deep understanding of this system and beneficial to process scale up for industrialization.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Salting-out extraction systems (SOESs) were first reported in 1973, in which an acetone-rich top phase and a salt-rich bottom phase were formed when salts were introduced into the aqueous solution of acetone [1]. It resembles aqueous two-phase systems (ATPSs) composing of polyethylene glycol (PEG), hydrophilic ionic liquid (IL) or surfactant and salts [2]. However, the phase separation in SOESs is mainly attributed to the salting-out effect. Compared to the traditional liquid–liquid extraction (water-immiscible organic solvents) systems, an important feature of SOESs is the high polarity of top phases (methanol, ethanol, acetone and acetonitrile), and thus it is useful for the extraction of polar solutes such as water-soluble alcohols and acids.

SOESs possess the advantage of large throughput, fast phase separation, continuous operation, low energy consumption and

high efficiency. Additionally, the possibility of recycling phase-forming components (hydrophilic organic solvent and salt) makes salting-out extraction a promising and sustainable downstream method [3–5]. The application of salting-out extraction for the bio-based chemicals has been recently reviewed in detail [2]. SOESs have also been used in the recovery of proteins [6,7], enzymes [4,8] and natural products [9–11]. However, even though a great amount of reports have been published on the separation of diverse target products with high partition coefficient and recovery on the laboratory scale, this technology has not been used in industrial scale, partially due to the limited engineering knowledge and understanding of this system.

Almost all of the batch extraction experiments were conducted following an empirical procedure (centrifugation, settling overnight or achieve complete phase equilibrium) without considering the time of the phase separation process [5–8,10–12]. However, these data are necessary for industrial application because the rate of phase separation determines the equipment design and thus the operation costs.

The progresses on phase separation for PEG–salt ATPS has been reviewed [13]. It has been reported that the phase separation time

was closely related to the composition of the system and phase continuity, which influenced the movement and coalescence of the droplets [14]. A mathematical model was also proposed to correlate the physico-chemical properties (viscosity, density and interface tension) and the phase separation rate in PEG–phosphate system [15]. However, to our knowledge, no systematical study has been reported on the separation rate in hydrophilic organic solvent-based SOESs.

In this work, phase separation time for the salting-out extraction system of ethanol–ammonium sulfate was studied in test tubes of different sizes at different mixing intensities by using a vortex mixer. The effects of tie line length, phase volume ratio and phase inversion point on the phase separation rate and the time for product distribution and phase equilibrium were also studied and are reported in this paper. This study provides insight into the phase separation kinetics needed for the design of appropriate extraction separators for SOESs.

2. Materials and methods

2.1. Materials

All the chemicals (ammonium sulfate, ethanol and butanol) were of analytical grade. Deionized water was used throughout the experiment.

2.2. Phase diagram and system composition

The binodal curve of ethanol–ammonium sulfate was obtained by cloud point method. For determination of the tie lines, the compositions of top and bottom phases were analyzed. The midpoint compositions of three tie lines were chosen as stock solution (Table 1).

2.3. Phase inversion point and phase continuity

Phase inversion point is where the continuous phase changes to dispersed phase and vice versa under certain conditions (at different phase volume ratios and degrees of mixing). Phase continuity can be detected through visual observation during the phase separation process, ascending droplets as continuous bottom phase and descending droplets as continuous top phase.

2.4. Batch experiments

Batch experiments were carried out in 10 mL graduated test tubes (0.2 ml) unless otherwise noted. The stock solutions representing the compositions of different tie lines were prepared by mixing predetermined weights of ethanol, ammonium sulfate and deionized water (Table 1), followed by thoroughly shaking and then settling for complete separation (overnight). Different proportions of top and bottom phases along the same tie line from said stock solution were mixed with Fisher Vortex Genie 2 at a high frequency (6) for 3 min. Test tubes of different sizes (10, 25 and

50 ml) were used and the frequency of vortex mixer was changed (from 1 to 6) to investigate their effect on the phase separation.

The separation time under gravity for each mixture was defined as the time when a clear interface was formed and determined by visual observation. Triplicate experiments were carried out. Butanol solution (20 g/L) was used to determine the time for product distribution and phase equilibrium.

2.5. Analytical methods

The concentration of alcohols was determined by gas chromatography (SHIMADZU GC-2010) equipped with a FID detector and a glass column packed with Chromosorb 101 (2 m × ϕ5 mm), and the ammonium sulfate concentration was determined by conductivity meter (DDS-307, Leici, China). Phase viscosity was measured by Brookfield DV-E viscometer at room temperature.

3. Result and discussion

3.1. Effect of system composition on the time of phase separation

Phase separation includes two steps: the droplets ascend or descend to the interface and the droplets burst and join its phase (known as the coalescence process). The movements of droplets depend on the balance of gravitational, flotation and frictional forces in the two phases [14]. The time of phase separation under gravity follows the Stokes law. So the sedimentation rate is determined by the droplet diameter, density difference and viscosity of the continuous phase [16].

In order to study the effect of system composition and physical parameters on the rate of phase separation, the physical parameters at different tie line lengths used in this study were measured (Table 2). As the tie line length increased from 42.5% to 56.6%, the compositions of both ethanol and ammonium sulfate in the top and bottom phases increased by 20% (Fig. 2). As a result, the phase separation rate was increased because of the increased salting-out effect and the polarity divergence between the two phases. Additionally, the densities and viscosities of two phases in SOESs were very similar, which was its significant character compared with traditional ATPSs [17]. The phase densities and viscosities of the top and bottom phases were close and the increased density difference (0.199–0.253 vs. 0.0379–0.0622 in PEG–phosphate system [16]) as the tie line length increased accelerated the phase separation process. However, the viscosity difference was not obvious, while in traditional ATPSs, the viscosity difference between the top and bottom phases was very large (5–50 times vs. ~1 in SOESs) [13]. It was clear from the data that the viscosity of top phase in ethanol–ammonium sulfate system (2.941–3.148 mPa s) was far less than that in the PEG–phosphate system (7.19–19.89 mPa s) [16], which was the major reason for the difference in phase separation time of these two systems.

The time of phase separation was recorded at three tie line lengths and at various phase volume ratios (from 1:9 to 9:1). Fig. 1 shows the effects of tie line length and phase volume ratio on the separation time. The phase separation time decreased as

Table 1
Tie lines data for the system of ethanol (1) + ammonium sulfate (2) + water (3) at temperature of 293.15 K.

Tie line	Tie line length (%)	Midpoint composition (w/w)		
		$w_1 \cdot 10^2$	$w_2 \cdot 10^2$	$w_3 \cdot 10^2$
1	42.5	27.002	17.368	55.630
2	51.4	29.524	18.252	52.224
3	56.6	29.928	19.122	50.950

Table 2
Physical parameters for ethanol–ammonium sulfate SOES at different tie line lengths.

Tie line	Density (g/cm^3)		Density difference	Viscosity (mPa·s)		Viscosity difference
	Top	Bottom		Top	Bottom	
1	0.937	1.136	0.199	3.148	3.083	−0.065
2	0.922	1.148	0.226	2.898	2.886	−0.012
3	0.912	1.165	0.253	2.941	2.968	0.027