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Liquid–liquid equilibrium of 1-butanol + water + tri-n-butyl phosphate + ammonium chloride system

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ABSTRACT

In this paper, the liquid–liquid equilibrium (LLE) and tie-line data of the system containing 1-butanol + water + tri-*n*-butyl phosphate (TBP) + ammonium chloride have been studied at 298.15, 308.15 and 318.15 K under atmospheric pressure. The influence of temperature and different concentrations of ammonium chloride have been investigated. In addition, nonrandom two-liquid (NRTL) model is applied to the system, and the relevant interaction parameters are regressed with the experimental data. The quality of the correlation is measured by the rmsd (rmsd $\leq$ 0.0131). The results show that the calculated values by NRTL model are in agreement with the determination of LLE data of the studied system in the investigated conditions.

1. Introduction

Tri-n-butyl phosphate (TBP) is widely used in the chemical industry as extractants, polymerization inhibitors, defoamers, solvents, etc. It can especially be used as a plasticizer with a special use as a solvent for the extraction of uranium and plutonium from other radionuclides in nuclear fuel reprocessing [1]. Conventionally, tri-*n*-butyl phosphate (TBP) is manufactured by the esterification process of excess 1-butanol and phosphorus oxychloride. In the process, ammonia is used to neutralize the large amounts of hydrochloric acid generated from the esterification. The by-product ammonium chloride, which is removed from the system, can be sold as chemical products after separation and purification. Then, the rest of the organic phase is refined via dealcoholization and water-washing to obtain pure tri-*n*-butyl phosphate. Finally, we may get a mixture of 1-butanol/water/tri-*n*-butyl phosphate/ammonium chloride. Since high purity TBP is what we wanted in this system, the research on the refinement of TBP becomes more necessary. In the producing process of TBP, the separation and purification of 1-butanol/water can directly affect the costs and quality of production, meanwhile the recovery of 1-butanol also has a major influence on environmental protection and resource utilization, since the potential of butanol is either as fuel or feedstock for industries [2].

The successful implementation of the above processes depends on the accurate LLE data. The studies on liquid–liquid phase equilibrium of aqueous–organic mixtures are also significant in scientific research and some chemical processes, such as the extraction process, the recovery of the organic compounds from the biomass fermented liquid, the simulation and optimization of the extraction process [3]. So far, lots of researchers have already investigated liquid–liquid phase equilibrium of different kinds of alcohol–water systems [4–6]. The presence of a salt or a non-volatile solute in a solvent mixture can significantly change its equilibrium composition [7]. About quaternary liquid–liquid phase equilibrium, there are few related literatures. Pereira and Aznar [8] have determined the system of water–2-propanol–1-butanol–KBr/$MgCl_2$ at different temperatures. Santos et al. [9] have studied the salt effect on liquid–liquid equilibrium of water + 1-butanol + acetone system. After comparing the ternary system without salt and the quaternary, they have found that the separation of alcohol–water system would be easier with the presence of salt. What Chen et al. [10] have shown is the liquid–liquid equilibrium for saturated aqueous solution of glycerol + 1-butanol + water + sodium chloride at different temperatures. The common point of these systems is that the effect of salting out must have been considered. Pirahmadi et al. [11] have made the LLE data of 1-butanol + water + NH_4Cl at different temperatures. It shows a good salting out effect in the two-phase region by adding ammonium chloride, while temperature has a minor effect on the liquid–liquid equilibrium in the studied temperature

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range. Yet, the phase equilibrium data of the 1-butanol/water/tri-*n*-butyl phosphate (TBP)/ammonium chloride (NH_4Cl) system have not been reported.

In this work, the liquid–liquid phase equilibrium data of 1-butanol/water/tri-*n*-butyl phosphate/ammonium chloride have been determined at 288.15 K, 303.15 K, 323.15 K, and 303.15 K for different contents of ammonium chloride. The experimental tie-line data has also been correlated with the nonrandom two-liquid (NRTL) model [12].

2. Experimental sections

2.1. Chemical reagents and instruments

All of the chemicals used in this study were of analytical grade without further purification. The gas chromatography was used to check the purity of these substances in this study and NH_4Cl needed a drying via vacuum drying oven (DZF-6020, Keelrein Instrument Co., Ltd.). The suppliers and mass fraction of the chemical reagents were given in Table 1. All of the mass determinations were carried out using an electronic analytical balance accurate to within ±0.0001 g (Sartorius analytical balance, BSA224S). Ultrapure water (Aquapro RM-220, Ever Young Enterprises Development Co., Ltd.) was used in all experiments. The experiments were carried out using a constant-temperature water bath oscillator (type HZS-H, Harbin Donglian Electronic Technology Development Co., Ltd.) with a water thermostat.

The measured and literature data of the CAS number, molar mass, boiling temperature, density, and refractive index for all of the materials used in the study at 293.15 K and atmospheric pressure were listed in Table 2. The refractive indexes of all the chemicals were measured by the Abbe refractometer (WAY-2S, Shanghai Shenguang Instrument Co., Ltd.), and the Ostwald-Sprenge pycnometers were used to measure densities [13].

The NH_4Cl concentrations in both phases were measured using an automatic titrator with volumetric titrations (916 Ti-Touch, Metrohm AG). The water concentrations in both phases were measured by the Karl Fischer titrimetric method [15] using a moisture analyzer with volumetric titrations (803 Ti-Stand, Metrohm AG), Karl Fischer reagent (KFR-06, Tjshield Co., Ltd.). The mass fractions of 1-butanol in the organic phase were determined by a gas chromatograph and pentanol known masses were added to each sample as the internal standard [11]. The GC-122 gas chromatograph was produced by Shanghai Precision & Scientific Instrument Co., Ltd. Hydrogen was produced by HGH-500E hydrogen generator that came from Beijing Huilong Company.

2.2. Procedures and methods of analysis

The quaternary LLE system was studied at different temperatures (288.15 K, 303.15 K, 323.15 K). We could observe the effect of temperature on LLE phase diagrams. The known concentrations of 1-butanol, water, tri-*n*-butyl phosphate and NH_4Cl were mixed in a conical flask. The mixture was shaken vigorously for 10 h in a constant-temperature water bath oscillator, and then settled at least 12 h to complete the separation of the phase at a constant temperature. In this work, the samples with various concentrations of salt were also measured to study the influence of salt concentration.

In each system, the mixture split into two immiscible phases. The top phase was the organics-rich phase with little amounts of dissolved salt and the bottom phase was the water-rich phase with a lot of dissolved salt, as a result of the large difference between the solubility of salt in 1-butanol and water. The aqueous solutions were removed from the bottom of the separatory funnel as aqueous samples, and the organic solutions left in the separatory funnel were taken as organic samples. Then the mass in each phase should be measured precisely. At last the samples of the top and bottom phases were taken for analysis.

The water was measured by the Karl Fischer titrimetric method [15]. The standard uncertainty of the determination was 0.003 by this method. The NH_4Cl concentration was measured with an automatic titrator. The standard uncertainty of the determination was 0.007 by this method. The gas chromatograph was used to analyze the 1-butanol composition in the organic phase. Uncertainty of GC analysis averaged 0.007. The gas chromatograph was equipped with a flame ionization detector. The length of the column packed with AT.SE-54 was 30 m. The flow rate of hydrogen used as the carrier gas was set to 40 cm^3/min. Temperature-programmed technique was adopted and the heating rate was 20 °C/min. The first section of the injector was filled with silica wool in order to avoid influx of the salt into the column. Each sample was preprocessed before injection. The organic phase was dehydrated by a 5A molecular sieve. Pentanol known mass was added to each analyzing sample as the internal standard, finally using the standard curve of pentanol and 1-butanol constructed previously to calculate the 1-butanol concentration of samples. The tri-*n*-butyl phosphate concentrations in both phase and the 1-butanol in aqueous phase were then determined by material balance [16,17]. Each sample in both layers was analyzed more than three times, and the average value was taken. The concentrations and the peak area of all the matter could be obtained from N-2000 data stations developed by Zhejiang University.

All of the concentrations in the tables were determined and reported as mass percentages, w_i^p, where p denoted the phase (p = a

Table 1
Suppliers and mass fraction of the chemical reagents.

Component	Supplier	Mass fraction	Analysis method
1-Butanol	Chengdu Kelong Chemical Reagent Co., Ltd.	0.995	GC[a]
Tri-n-butyl Phosphate	Chengdu Shifang Zhongcui Chemical Co., Ltd.	0.995	GC[a]
NH_4Cl	TianJin Meilin Chemical Holding Co., Ltd.	–	

[a] Gas chromatograph.

Table 2
CAS number (CAS), mole weights (M), boiling temperatures (*bp*), densities (ρ) and refractive indices (n_D) at T = 293.15 K and p = 1.013 bar[a].

Component	CAS	M (g/mol)	bp (K)	ρ(g/cm^3)		n_D^{20}	
			Lit [14]	exp	Lit [14]	exp	Lit [14]
Water	7732-18-5	18.00	373.15	0.998	0.998	1.3328	1.3330
1-Butanol	71-36-3	74.12	390.85	0.810	0.811	1.3393	1.3393
Tri-*n*-butyl Phosphate	126-73-8	266.32	562.15	0.976	0.977	1.3989	1.3993
NH_4Cl	12125-02-9	53.49	793.15	1.527	1.527	1.6380	1.6420

[a] Standard uncertainties u are $u(\rho)$ = 0.006 g/cm^3, $u(n_D^{20})$ = 0.0001.