



Solubility and partition coefficient of p-toluic acid in p-xylene and water

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ABSTRACT

The solubility and partition coefficient of p-toluic acid in p-xylene and water at ambient pressure were measured over the temperature range of 303.2–353.2 K. The measured solubility data and partition coefficient data were well correlated by the NRTL equation. The well-documented p-toluic acid–water system was used to validate the reliability of the sampling and analytical techniques employed. The results showed that the solubility of p-toluic acid in p-xylene and water increases with the temperature increase. The partition coefficient of p-toluic acid between p-xylene and water increases with the increasing initial mass of p-toluic acid, but decreases with the rising temperature. The equilibrium data of the ternary system are essential for the extraction process design and scale-up in the PTA wastewater recovery and treatment.

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1. Introduction

Purified terephthalic acid (PTA) is one of the most important raw materials for polyester produce [1,2]. When the terephthalic acid crystals are washed, the wash water carries away unwanted aromatic acids byproducts, such as p-toluic acid, benzoic acid, isophthalic acid, terephthalic acid, trimellitic acid and o-phthalic acid. PTA manufacturing plants generate large amounts of wastewater and environmental control standards prevent the discharging of the untreated water into natural waterways [3,4].

Currently, the treatment method of PTA wastewaters involves the biological anaerobic [3–11] and aerobic [12–14] technologies. The pollutants in PTA wastewater are removed by retaining the water in biological lagoons for extended periods of time, whereby microbial action reduces the pollutants to innocuous constituents. However, the traditional treatment is expensive and inefficient, and has failed to enable reuse of and byproduct components and recovery of the water [12,13,15–21]. Some physico-chemical treatment methods are reported such as oxidation processes [16,22], adsorption [18,19] and coagulation and flocculation [23,24]. But physico-chemical treatments are more expensive and lead to a secondary pollution [25].

Accordingly, there exists a need for an improved method for treating PTA wastewater. The p-xylene extraction method may be one of the alternative methods. As p-xylene is the raw material in PTA process, and p-toluic acid is the intermediate, the extract phase dissolved recovered aromatic acids could be directed to

the oxidation reactor after the extraction. The method should be more efficient and economical, and enable the recycling of the water and recovery of valuable components from the wastewater. Numata and Takahashi [26] designed the extraction process. The wastewater were cooled down and filtered out the aromatic acid precipitation, and then extracted with p-xylene in the extraction column, where agitator was used to enhance extraction mass transfer. However, it is hard to avoid that the emulsified p-xylene could be lost with water during the oil-water decantation process, and required a more efficient extraction process.

Authors [27] have studied the non-dispersive solvent extraction (NDSX) method to recovery the aromatic carboxylic acids from PTA wastewater. So far, the applications of NDSX techniques have been studied in the treatment of large volumes of the effluents generated by chemical industries [28–32]. The non-dispersive solvent extraction (NDSX) may be a more promising technology for PTA wastewater treatment. Using a hollow fiber membrane contactor, the organic and aqueous phases in the NDSX process contact through inert surface without turbid dispersion [33]. Therefore, the emulsified probability of p-xylene could be avoided and the NDSX extraction process would be more efficient.

In the published literature, there are some experimental solubility and partition coefficient data on p-toluic acid published, such as solubility in N,N-dimethylformamide [34], N-methyl-2-pyrrolidone, N,N-dimethylacetamide, chloroform, acetic acid, water [35–37] and partition coefficient between octanol and water [38]. However, the partition coefficient of p-toluic acid between p-xylene and water is few. Only one at 369.15 K was reported by Petty-Weeks and Zeitlin [39]. However, the NDSX process of PTA wastewater is carried out at 327–331 K usually [40]. The equilibrium data of this ternary system at the temperature 327–331 K

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Table 1
Sample description table.

Chemical name	Source	Mass fraction purity
p-Toluic acid	Shanghai Fei Xiang Chemical Co.	≥0.99
p-Xylene	Sinopharm Chemical Reagent Co. Ltd.	≥0.99
Methanol	Tedia Company Inc.	≥0.999
Acetonitrile	Tedia Company Inc.	≥0.999

are essential for the extraction process design and scale-up. In this work, the solubility of p-toluic acid in p-xylene and water and partition coefficient between p-xylene and water were measured for the first time in the temperature range from 303.2 to 353.2 K. The experimental solubility data and partition coefficient data were correlated with the NRTL activity coefficient model. The results show that it is possible to treat p-toluic acid in PTA wastewater by using p-xylene. The experimental data and correlation equation could be used for industrial applications and operation optimization.

2. Experimental

2.1. Materials

Chemicals are listed in Table 1. Deionized water was used throughout all the experiments. All the chemicals were used as received without further purification.

2.2. Apparatus and procedure

The experiments were carried out at ambient pressure in a jacketed equilibrium glass vessel with a working volume of 100 mL for solubility experiments and 250 mL for partition coefficient experiments. In the whole experiment process, the glass vessel was sealed by a rubber stopper to prevent the evaporation of solvent and was put in a thermostatic water circulator bath. The bath was continuously mechanically stirred, and the temperature in the glass vessel was controlled within ± 0.1 K of the desired one with a thermoelectric controlling system.

The solubility was measured by static analytical method. The saturated solutions for the experiments were prepared by adding excess amount of p-toluic acid. Samples were weighted by an analytical balance and put into the vessel. Then, the glass vessel was heated to a constant temperature. The initial equilibrium time of the saturated solution was 24 h, and then it was sampled once for 3 h until the results of solubility data were reproducible within 3%. It was found that 36 h was enough for p-toluic acid in water and p-xylene to reach equilibrium. The syringes used to sample the liquid phase were preheated to prevent the crystallization of p-toluic acid in saturated solution. A preheated 5 mL syringe with a needle introduced through the rubber stopper to withdraw about 2 mL of clear upper portion of the p-xylene or water phase each time. In this way, there was no leakage of the solution in the whole sampling process. As soon as possible, the sampled solution was transferred into a test tube which had already contained about 3 mL of methanol. The added methanol decreased the temperature of the sample to prevent its vaporization. Then, the syringe was washed ten times by methanol to make sure the minute quantity sample residual in the syringe was washed clean, and the washings were collected together in the same test tube. The sample and the washings were all weighted by analytical balance, respectively. The sampling tubes were sealed without the leakage of the samples and they would be analyzed within 6 h. Three parallel samples were obtained for each temperature in the solubility experiments to make the data more reliable.

The partition coefficient of p-toluic acid between p-xylene and water were determined by adding certain amount of p-toluic acid (less solubility in p-xylene at a temperature) in the jacketed equilibrium glass vessels with a magnetic stirrer. Then with p-xylene and deionized water mixtures of fixed mass ratio, the agitation was started. The rotation speed of the magnetic stirrer was about 700 r/min to make sure the two-phase mix well.

The initial amount of both p-xylene and deionized water added into each bottle was 50.00 g. After at least 2 h, the agitation was stopped, and the solution was kept still for 24 h. Then following de Doz et al. [41], a preheated 5 mL syringe with a needle introduced through the rubber stopper to withdraw about 2 mL of upper organic phase. Samples of the lower phases were then obtained by introducing the needle and blowing air through it while it went through the upper phase, to avoid its contamination. Then, the needle was separated from the syringe to make sure the sample in the syringe was not contaminated when it was poured into the test tube. As soon as possible, the sampled solutions were placed into test tubes which had contained methanol. The following processes to treat the samples were just the same as the process of solubility experiments.

2.3. Analytical method

The concentrations of p-toluic acid in solutions and p-xylene in water were determined by HPLC (Agilent 1100 Series). A Diamondsil C18 (250 mm \times 4.6 mm) chromatographic column was used. The internal standard method was used in the analysis of solubility in p-xylene, and p-xylene itself was used as internal substance. Distinct from solubility in p-xylene analysis, an external standard method was used in the solubility in water and partition coefficient measurement because of the much smaller concentration of the solute in the mixture.

Gradient elution was used, mobile phase consisted of water, methanol and acetonitrile, and the following mass fraction of a three-component gradient elution program was adopted: from 0 to 3 min, the mixture mass fraction changed linearly with time from 45% methanol, 45% water and 10% acetonitrile to 95% methanol and 5% acetonitrile; from 3 to 6 min, the mixture mass fraction was not changed. Each analysis took about 9.0 min. The flow rate of the elution solvents is 1.500 mL min⁻¹. The DAD signal wavelengths for p-toluic acid and p-xylene were 254 nm and 269 nm respectively to get strongest signal responses.

An analytical balance (FA2104N Shanghai Mingqiao Precision & Scientific Instrument Co. Ltd.) with an accuracy of ± 0.0001 g was used for both the calibration curves and the analysis of the unknown samples. Table 2 shows the experimental masses of the components that were used to obtain the calibration curves for p-toluic acid and p-xylene with the external method and p-toluic acid with the internal method. The compositions in mole fractions were measured with an experimental uncertainty of ± 0.0005 .

3. Results and discussion

3.1. Solubility data

The measured solubility data of p-toluic acid in p-xylene and water were listed in Table 3 where x was the mole fraction of p-toluic acid. The relative deviations of three parallel samples for each temperature were within $\pm 3\%$. As can be seen from Fig. 1 that within the temperature range of the measurements the solubility of p-toluic acid in p-xylene and water showed an increasing trend as the measured temperature increased.

The solubility data in water are much smaller than in p-xylene at constant temperature. This phenomenon may be explained by the

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