



## Partitioning of diuron in a novel aqueous two-phase system based on polyols and tetrahydrofuran



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### ABSTRACT

Diuron is an herbicide widely used in agriculture as a soil sterilant to control a large variety of weeds. This compound is considered moderately toxic and dangerous to the environment. This study examined the formation of an aqueous two-phase system (ATPS) based on tetrahydrofuran (THF) and polyols (glycerol, erythritol, xylitol, sorbitol and maltitol) in order to promote a simple recovery method that is low cost since diuron can be found in the uptake of water for human consumption. The binodal curves were determined at 25 °C and atmospheric pressure. The ability of the polyols to promote the formation of ATPS with THF preferably occurred in the growing direction of hydroxyl groups, glycerol (3-OH) to maltitol (9-OH). To explore the differences induced by the presence of the distinct polyols, the partition behavior of diuron was monitored by determining of the partition coefficient ( $K_{Diu}$ ) and recovery in the top phase ( $R_T$ ). In all systems, THF was in the top phase and the polyols in the bottom phase. Preferably, diuron was best partitioned to the top phase ( $K_{Diu} \approx 20$  and  $R_T \approx 93$ ) due the effect salting-out caused by maltitol on the diuron molecules.

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## 1. Introduction

Diuron (*N*-(3,4-dichlorophenyl)-*N,N*-dimethyl-urea) is one of the most widely used herbicides, particularly in agriculture as a soil sterilant in order to control a wide variety of weeds, annual and perennial grasses, and mosses [1–3]. The diuron (*N*-(3,4-dichlorophenyl)-*N,N*-dimethyl urea) molecule has moderate water solubility (42 mg L<sup>-1</sup> at 20 °C) and belong to the family and subclass of phenylureas phenylamide [4]. The use of this compound as herbicide can contaminate soil, ground and surface water by runoff and percolation [1,2,5], consequently contaminates water supplies and generates health risk. Diuron concentrations (0.9 ng L<sup>-1</sup>) were detected in water collection points for public supply, values that are above international standards (0.1 ng L<sup>-1</sup>) [6]. Therefore, the development of protocols for diuron extraction and concentration for posterior detection is necessary.

Several techniques have been used for detection of these

compounds, such as gas and liquid chromatography, electrochemical sensor and fluoroimmunoassay techniques, which present detection limits between 100 and 0.1 ng L<sup>-1</sup> [7–9]. All these methods are expensive, due to either the need for concentration of the sample or the sophistication of the analysis method. An alternative to diuron recovery and concentration is the use of new technologies such as aqueous two-phase systems (ATPS), consisting of different compounds that had not been reported in the literature. Dinis et al. [10] used ATPS for concentration of pollutant ethinylestradiol, reaching concentration up to 1000-fold (from ng L<sup>-1</sup> to µg L<sup>-1</sup>) higher than those found in wastewater.

ATPS are composed of two immiscible aqueous liquid phases macroscopic in concentrations higher than the critical concentration of each component, when they are dissolved in water. The scientific literature describes studies on the application of ATPS for the extraction and purification of biomolecules such as antibiotics [11], anthocyanins [12], amino acids [13], proteins [14] and enzymes [15–17]. These systems have some advantages such as versatility, high efficiency, fast mass transfer rates, low cost and ease operation and scale up [18]. The first systems consisted of two aqueous mixtures of polymer-polymer or polymer-salt [19,20]. Therefore, these systems had their applicability restricted due to

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the limited range of polarities, leading to the development of new systems formed by different constituents such as ionic liquids [22,23], organic solvents, for example alcohols [24,25], acetonitrile [26–28] and tetrahydrofuran [29–31], as well as ionic liquids as adjuvant of phase formation [32,33].

In this sense, the tetrahydrofuran (THF) is an aprotic organic solvent, moderately polar (logarithm of octanol-water coefficient  $-\log K_{ow} = 0.46$ ) and completely soluble in water at room temperature. This solvent is used in the manufacture of materials for packaging, transport and storage of food, as well as a solvent for paints and varnishes [34,35]. Recently, THF was described as able to form ATPS and purify lipolytic enzymes obtained via submerged fermentation [29,30].

Polyols are a special class of carbohydrate and may be mono-saccharides (e.g., sorbitol, mannitol, xylitol and erythritol), disaccharides (e.g., maltitol, lactitol and isomalt) or mixtures of polysaccharides and hydrogenated saccharides [36]. The polyols or polyhydric alcohols differ from other saccharides due to the reduction of ketone and aldehyde functions. These compounds are used in various areas, including food, pharmaceuticals and cosmetics [37,38], and are also considered a new-generation green energy platform. Thus, in order to develop new ATPS more economically and efficiently, these will be used for the first time to form systems with THF.

Therefore, this work focuses on the design of ATPS based on tetrahydrofuran (THF) and polyols (glycerol, erythritol, xylitol, sorbitol and maltitol), assessing the structure of the compounds for the ability to induce the formation of two aqueous phases. Finally, the applicability of these ATPS, concerning the ability of different polyols to induce partitioning of the diuron was explored. Note that diuron is a hazardous pollutant due to its carcinogenicity [3], and therefore, the development of techniques leading to easy recovery and concentration and sequential quantification is paramount.

## 2. Materials and methods

### 2.1. Materials

The systems studied in this work were formed by different polyols and tetrahydrofuran (THF). All polyols were purchased from Sigma-Aldrich®: glycerol (purity  $\geq 99.5\%$ ), erythritol (purity  $\geq 99\%$ ),

xylitol (purity  $\geq 99\%$ ), sorbitol (purity  $\geq 98\%$ ) and maltitol (purity  $\geq 98\%$ ), as present in Table A1 Supporting Information. The molecular structures of the polyols studied are shown in Fig. 1. THF (HPLC grade, 99.9% purity) and diuron (purity  $\geq 98\%$ ) were also purchased from Sigma-Aldrich®. Deionized water was used in all experiments.

### 2.2. Phase diagrams and tie-lines

The phase diagrams were determined for each polyol and THF at  $25 \pm 1$  °C and atmospheric pressure by applying the cloud-point titration method [27,30]. Stock solutions of polyols ( $\approx 30$ – $80$  wt %) depending on the solubility of the carbohydrate in water and THF ( $\approx 80$  wt%), were previously prepared and used for determination of phase diagrams. This procedure was repeated to obtain sufficient data for the construction of a liquid–liquid equilibrium binodal curve. The compositions were determined by the weight quantification of all components added within an uncertainty of  $\pm 10^{-4}$  g. The binodal curve data were correlated using Eq. (1) [39].

$$[\text{Polyol}] = A \exp \left[ \left( B[\text{THF}]^{0.5} \right) - (C[\text{THF}])^3 \right] \quad (1)$$

where [Polyol] and [THF] are mass fraction percentages of polyols and THF, respectively; and A, B and C are the regression constants.

The experimental tie-lines (TLs) were measured with the procedure outlined in our previous work [29], and the equations are described in the Supporting Information. For the determination of TL composition, different mixing points in the two-phase region was prepared, vigorously shaken, centrifuged at 3000 rpm for 10 min (for acceleration of the phase separation) and allowed to stand to reach thermodynamic equilibrium (for at least 18 h and at 25 °C). After equilibration, the top and bottom phases were separated and weighed and the volume determined. It should be considered that for systems composed of THF + a polyol, the bottom phase is the polyol-rich phase, whereas the top phase corresponds to the THF-rich phase.

The tie-line lengths (TLLs) were determined through the application of Eq. (2), which uses the concentrations of [THF] and [Polyol] in the two phases.

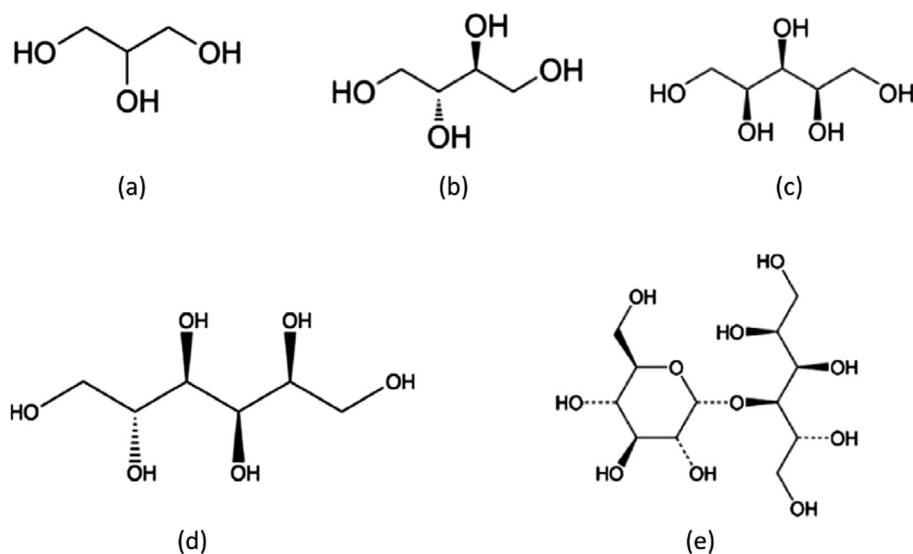


Fig. 1. Molecular structure of the polyols with (a) glycerol, (b) erythritol, (c) xylitol (d) sorbitol and (e) maltitol.

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