



# Novel phase diagrams of aqueous two-phase systems based on tetrahydrofuran + carbohydrates + water: Equilibrium data and partitioning experiments



Kênia M. Sousa<sup>a</sup>, Gustavo E.L.O. Maciel<sup>a</sup>, Filipe S. Buarque<sup>a</sup>, Adriana J. Santos<sup>b</sup>,  
 Maria N. Marques<sup>a,b</sup>, Eliane B. Cavalcanti<sup>a,b</sup>, Cleide Mara F. Soares<sup>a,b</sup>, Álvaro S. Lima<sup>a,b,\*</sup>

<sup>a</sup> Universidade Tiradentes, Av. Murilo Dantas 300, Farolândia, CEP: 49032-490, Aracaju, SE, Brazil

<sup>b</sup> Instituto de Tecnologia e Pesquisa, Av. Murilo Dantas, 300, CEP: 49032-490, Aracaju, SE, Brazil

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## ABSTRACT

This work addresses the partitioning of diuron, a herbicide heavily employed in agriculture, using the aqueous two-phase system formed by tetrahydrofuran and carbohydrates. Phase diagrams using tetrahydrofuran (THF) and six monosaccharides, two disaccharides and three commercial sugars at 298.15 K and 0.1 MPa were constructed. The equilibrium phases were further characterized by determining the density and viscosity at 283.15–333.15 K and 0.1 MPa. Finally, the diuron extraction was assessed by the partition coefficient ( $K_{DIU}$ ) and recovery in the top-phase ( $R_T$ ). The number of equatorial hydroxyl groups present in the carbohydrates' structures is the driving force for the phase separation; disaccharides are stronger inducers of the ATPS formation than monosaccharides. The differences in the density and viscosity of the phases allowed an easy phase separation. In all cases, the diuron partitions preferentially to the THF-rich phase with  $K_{DIU}$  ranging from 1.23 (commercial glucose) to 16.19 (pure glucose) and recovery between 49.45% (commercial glucose) and 92.70% (pure glucose), demonstrating the applicability in the partition of diuron.

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## 1. Introduction

Aqueous two-phase systems (ATPS) were first introduced by Beijernick in 1896 [1]. In the last few decades, they have become an option in liquid-liquid extraction systems due to their characteristics such as low interfacial tension and good mass transfer, which allow high yields; their environmentally friendly features (e.g., high water content); and the ease of scaling up [2,3]. A wide range of molecules have been successfully separated, recovered and purified using ATPS, such as enzymes (pectinase [4], lipase [5]), antibiotics [6], antibodies [7,8], alkaloids (gallic acid [9] and quinine [10]), metals [11], and dyes [12].

ATPS can be formed when two structurally different compounds are dissolved in water above a certain concentration [13]. The success of an ATPS depends on the choice of system constituents, which are usually two polymers (dextran + dextran,

dextran + polyethylene glycol (PEG), dextran + Ficoll and PEG/ maltodextrin [14,15]); polymer + salt (PEG + potassium phosphate [16]), and recently, ionic liquids + salts [17–21], ionic liquids + sugar [22], ionic liquids + PEG [23,24], organic solvents + salts (alcohol + potassium phosphate [25], organic solvents + carbohydrates/polyols) (acetonitrile + carbohydrates/polyols [26,27] and organic solvent + dextran [28]).

Recently, tetrahydrofuran (THF) has also been proposed as a constituent of ATPS [29,30]. THF ( $C_4H_8O$ ) is a cyclic ether that is miscible with water in all proportions at room temperature [31,32] and is highly flammable (flashpoint  $-21.2$  °C), with a vapor pressure of 21.6 kPa at 25 °C [33]. This organic solvent is employed as a solvent of dyes and lacquers, a precursor in the synthesis of succinic acid, a reaction medium, and a polymerization solvent for fat oils, among other applications [34].

The goal of this study is to associate carbohydrate and THF to develop a novel aqueous two-phase system for use in the partition of water-soluble herbicides such as diuron. It is well known that carbohydrates do not present any environmental or health concerns, and according to Banton and co-workers [33], THF does not

\* Corresponding author. Universidade Tiradentes, Av. Murilo Dantas 300, Farolândia, CEP: 49032-490, Aracaju, SE, Brazil.

E-mail address: [alvaro\\_lima@unit.br](mailto:alvaro_lima@unit.br) (Á.S. Lima).

have an adverse impact on human health and the environment. In animals, the acute toxicity potential is low to moderate by different routes. Although absorption through the skin is rapid, skin irritation is slight. Genetic toxicity has been negative, as well as reproductive toxicity, but it produces benign tumors in rats, which is not relevant to human health. Therefore, it can be said that the components of the system do not have any risk to human health and the environment. Thus, these ATPS based on carbohydrates and THF may be used for the separation, extraction/recovery or detection of diuron from aqueous media.

Diuron (N-(3,4-dichlorophenyl)-N,N-dimethyl-urea) is a crystalline compound belonging to the phenylamide group [35]. According to Giacomazzi and Cochet [36], diuron is a non-ionic and non-volatile substance whose melting point is 158–159 °C and water solubility is 42 mg L<sup>-1</sup>. Its octanol-water partition coefficient (log K<sub>ow</sub> = 2.6) characterizes it as a hydrophobic compound, which has been widely used in pre- or post-emergent treatment in agricultural crops [37]. The presence of diuron in drinking water and food is extremely harmful to human health due to its carcinogenicity [38], which makes this herbicide a dangerous aquatic pollutant.

## 2. Material and methods

### 2.1. Materials

Tetrahydrofuran - THF (HPLC grade, 99.9 wt%) was purchased from Sigma-Aldrich®. The carbohydrates used here were D-(+)-xylose (99 wt%), D-(-)-fructose (>98 wt%), L-(+)-arabinose (>99 wt%), D-(-)-arabinose (>99 wt%), D-(+)-mannose (>99 wt%), D-(+)-glucose (>95 wt%) and sucrose (>95.55 wt%). D-(+)-maltose (98 wt%) was purchased from Vetec®. The commercial sugars (viz. sucrose - Pinheiro®, glucose - Yoki® and fructose - Doce Menor®) were acquired from the local market in Aracaju-Sergipe, Brazil (Supporting Information Table A.1). Fig. 1 depicts the chemical structure of the compounds. Deionized water was used in all experiments.

### 2.2. Phase diagrams

This study concerns the measurement of novel phase diagrams for ATPS based on tetrahydrofuran and monosaccharides (D-(+)-xylose, D-(+)-fructose, L-(+)-arabinose, D-(-)-arabinose, D-(+)-mannose, D-(+)-glucose), disaccharides (D-(+)-sucrose and D-(+)-maltose), as well as commercial sugars (sucrose, glucose and

fructose).

The experimental data were determined gravimetrically, within an uncertainty of ±10<sup>-4</sup> g, by the cloud point method at 298.15 ± 1.00 K and 0.10 ± 0.01 MPa. This procedure follows a protocol already established in our previous works [25,26]. Aqueous solutions of carbohydrates (≈40–70 wt%) and tetrahydrofuran (≈80 wt%) were prepared. Drop-wise addition of the tetrahydrofuran was carried out to each solution of carbohydrate until the visual detection of a cloud point (biphasic region). Subsequently, drop-wise addition of water was performed until the solution became clear (monophasic region). This protocol was carried out under constant stirring and was repeated several times in order to obtain sufficient data for the construction of a liquid-liquid equilibrium binodal curve. The experimental binodal curves were adjusted to Merchuk's equation [39]:

$$[CAR] = A \times \exp(B[THF]^{0.5} - C[THF]^3) \tag{1}$$

where [CAR] and [THF] are, respectively, the carbohydrate and tetrahydrofuran mass fraction percentages, and A, B and C are the adjustable parameters.

Two mixture points in the biphasic region of the diagram phases were chosen. Initially, stock solutions of each carbohydrate were prepared, and subsequently, pure THF was added. The mixtures were vigorously stirred, and after reaching equilibrium (at least 12 h at 298.15 ± 1.00 K), the phases were carefully separated and weighed to within ±10<sup>-4</sup> g. To obtain the components' concentration in the top and bottom phases, Equations (2)–(5) were solved (mass balance), and the tie-lines were determined individually.

$$[CAR]_T = A \times \exp(B[THF]_T^{0.5} - C[THF]_T^3) \tag{2}$$

$$[CAR]_B = A \times \exp(B[THF]_B^{0.5} - C[THF]_B^3) \tag{3}$$

$$[CAR]_T = \left(\frac{[THF]_M}{\alpha}\right) - \left(\frac{1-\alpha}{\alpha}\right)[THF]_B \tag{4}$$

$$[THF]_T = \left(\frac{[THF]_M}{\alpha}\right) - \left(\frac{1-\alpha}{\alpha}\right)[THF]_B \tag{5}$$

where the subscripts “T” and “B” designate the top (tetrahydrofuran rich-phase) and bottom (carbohydrate rich-phase) phases, respectively, and “M” represents the mixture composition. The parameter

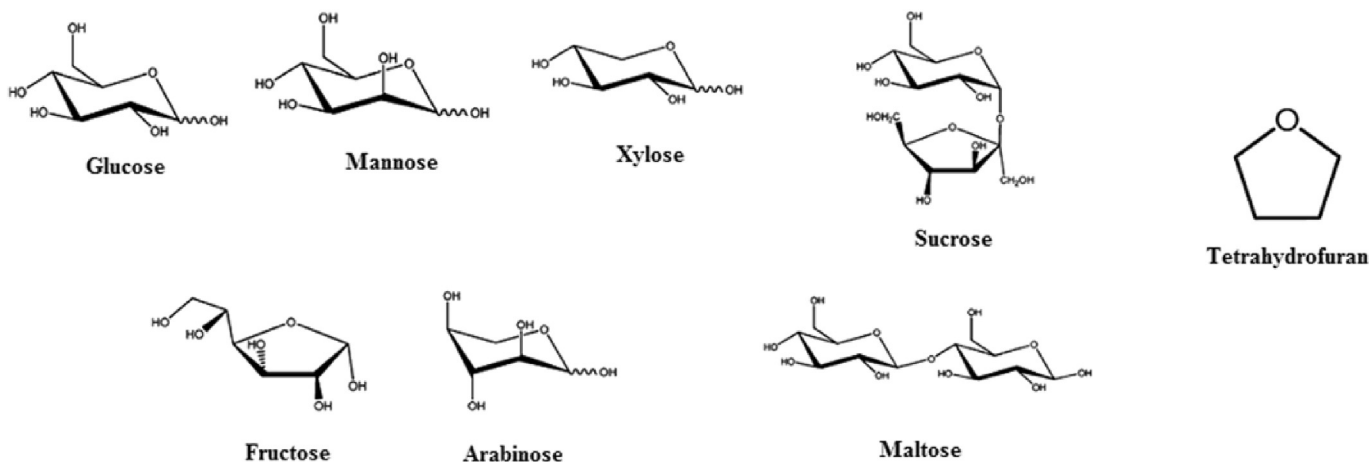


Fig. 1. Molecular structure of carbohydrates and tetrahydrofuran used to form aqueous two-phase system.

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