



# Aqueous solubility, vapor pressure and octanol-water partition coefficient of two phthalate isomers dibutyl phthalate and di-isobutyl phthalate contaminants of recycled food packages

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## ABSTRACT

In this work, we studied the aqueous solubility, vapor pressures of dibutylphthalate (DBP) and di-isobutylphthalate (DIBP) as a function of temperature between 298.15 and 328.15 K and between 313.15 and 423.15 K respectively. The octanol-water partition coefficient was measured at 298.15 K using shake-flask method. For aqueous solubility, measurements were carried out using the dynamic saturation method and values ranges in  $10^{-7}$  mol fraction with a relative higher solubility for DIBP regarding DBP. Solubility results are in good agreement with the octanol-water partition coefficient measurement showing that DBP is more hydrophobic than its isomer DIBP. For vapor pressure, after an interlaboratory validation step using static method performed with DBP in a temperature range between 381 and 421 K, measurements for both compounds DBP and DIBP using the gas saturation method presented a standard relative deviation lower than 2% and values ranged from  $10^{-2}$  and  $10^2$  Pa. By combining vapor pressure and solubility results, we calculated Henry's law constant and air-water partition coefficient and showed an important deviation between the two isomers even at low temperature.

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## 1. Introduction

The determination of physical-chemical and thermodynamic properties of chemicals are considered vital pre-requisites for accomplishing other tasks like, process design, simulation and computer aided molecular/mixture design [1]. They are also key parameters in the evaluation of their environmental fate and behavior in different compartments [2–6] and their distribution in food and bodies [7–9]. Therefore, many agencies like EU REACH established many regulations in order to classify chemical toxicity based on their intrinsic characteristics like physicochemical properties [10].

Phthalates has been the subject of research due to its huge volume of production, their wide applications and their high

environmental relevance [11]. Phthalates or phthalic acid esters (PAEs) are a group of plasticizers used since the 1920s as alternatives to the camphor before the synthesis of the polyvinylchloride (PVC) in 1930s. Since then, phthalates have been used increasingly even with other types of polymers like polyvinyl acetates (PVA), polyethylene (PE), cellulosic and polyurethanes to improve their performance in terms of flexibility, transparency, durability and longevity [7,12,13]. Phthalates are used intentionally in medical devices (intravenous bags and tubing), childcare materials (toys ...), household goods and food contact materials in addition of their use as solvent in personal care products (fragrance ...) and household products [14]. In general, the content of phthalates in different polymers varies from 10% to 60% by weight, and they are not covalently linked to the matrix [7], making their diffusion and release easier into their surrounding environment leading to the contamination of the air, soil and water as shown in several studies [15] before entering the food chain. In addition, phthalates are

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detected in recycled paperboard food packages at a higher level than virgin packages [16–18] and thus migration process to food matrices is another source to human exposure. Phthalates are classified as endocrine disruptors as a primary mechanism of action in addition to the numerous health problems as osteoporosis, reduction in body weight, skin and breast cancers, etc. [12].

The aim of this study is to extend the knowledge of phthalates in terms of physical chemical properties, specifically the dibutylphthalate (DBP) and its isomer di-isobutylphthalate (DIBP) since migration studies show their presence in multiple types of food packages virgin and recycled ones [19,20] in addition to their ubiquitous presence in the environment [15]. In this paper, we determined experimentally the aqueous solubility of both isomers DBP and DIBP (at 298.15–328.15 K), their vapor pressure (at 313.15–423.15 K) using the dynamic saturation methods, and their octanol/water partition coefficient  $\log K_{OW}$  at 298.15 K using the shake-flask method. From the latter determinations, we determined the environmental partitioning parameters namely, the Air-Water partition coefficient  $K_{AW}$  and Henry's constant  $K_H$ .

## 2. Materials

The compounds DBP, DIBP and BBP (butylbenzylphthalate) structures and CAS number are summarized in Table 1. DBP (99% purity), DIBP (99% purity) and BBP (98%) used as internal standard were purchased from Sigma-Aldrich and used without further purification. Methanol and acetonitrile (HPLC Grade) were provided by Sigma-Aldrich. Ultra-pure water was prepared on milli-Q purification system from Millipore.

## 3. Aqueous solubility

The measurement of the aqueous solubility is performed in order to compare the behavior of the two isomers DBP and DIBP in the aqueous phase.

### 3.1. Dynamic saturation method apparatus

The aqueous solubility of both compounds DBP and DIBP is measured by the dynamic saturation method in a temperature range between 298.15 K and 328.15 K, Fig. 1. The used apparatus has been described in detail in previous papers [21].

The principle of this method is based on the saturation of a known quantity of water flowing through a cell (b) packed with a stationary phase, Chromosorb W 60/80 mesh (Interchim, France), previously coated by the organic solute (>5% by mass). The saturated water flows into the extraction column (d) where the sample is trapped for analysis after a cooling step (c). Water exempt of solute is recovered in a flask for weighting (f). A liquid

chromatography pump assures water delivery at a low flow mL  $\text{min}^{-1}$  ensuring the liquid-liquid equilibria. Finally the solute is eluted from the cartridge by an adequate solvent (methanol) in order to perform a quantitative analysis by HPLC-UV.

There are several sources of uncertainty in the measurement of the aqueous solubility using the dynamic saturation method. One of the sources is the temperature uncertainty  $u(T) = 0.02$  K. Other source of uncertainties emerging from weighing and analysis procedures are presented as standard uncertainty ( $u(X)$ ) in Table 3.

### 3.2. Solubility of DBP and DIBP

The validation of the method is reported in previous papers [21–23]. For DBP and DIBP, aqueous solubility is measured in a temperature range of 298.15–328.15 K, and each measurement is repeated three times at atmospheric pressure. The analysis is performed by HPLC-UV using internal calibration method with BBP (butylbenzyl phthalate) as internal standard. The solubility is reported in mole fraction estimated from the following Eq. (1):

$$X = \frac{n_{\text{solute}}}{(n_{\text{water}} + n_{\text{solute}})} \quad (1)$$

with “X” the solubility in mole fraction and “n” the amount (mole) of the solute and water respectively.

The experimental data were fitted using Heidman's equation [24] Eq. (2):

$$\ln X = A + \frac{B}{T/K} + C \ln(T) \quad (2)$$

where X is the aqueous solubility in mole fraction, T the temperature in Kelvin, and A, B and C are the equation fitting parameters referring to each isomer. Using these parameters, the study of the thermodynamic changes occurring with Gibbs energy ( $\Delta_{\text{sol}}G^0$ ), molar enthalpy ( $\Delta_{\text{sol}}H^0$ ) and molar entropy of dissolution ( $\Delta_{\text{sol}}S^0$ ) of solution become easier.

By ignoring the effect of water dissolution in the solute phase, and assuming that both activity coefficient of water in aqueous phase and organic solute in organic phase are equal to 1, the molar enthalpy of dissolution ( $\Delta_{\text{sol}}H^0$ ) is obtained through Eq. (3) [25,26]:

$$\Delta_{\text{sol}}H^0 = RT^2 \frac{d \ln X}{dT} \quad (3)$$

Where ( $\Delta_{\text{sol}}H^0$ ) is the difference between the partial molar enthalpy  $H_i$  of component i in solution, and the pure molar enthalpy  $H_i^0$ , at a temperature T Eq. (4):

**Table 1**  
Structures and properties of phthalates.

Compound	Formula	CAS no	Molecular weight ( $\text{g mol}^{-1}$ )	Purity (% by mass)	Structure
DBP	$\text{C}_{16}\text{H}_{22}\text{O}_4$	84-74-2	278.343	99	
DIBP	$\text{C}_{16}\text{H}_{22}\text{O}_4$	84-69-5	278.343	99	
BBP	$\text{C}_{19}\text{H}_{20}\text{O}_4$	85-68-7	316.38	98	

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