



Enhanced partition model of 4-nitrophenol in water – octanol system. Effects of association/dissociation processes



Adriana Monica Radu, Ana Maria Josceanu^{*}, Daniel Dinculescu, Vasile Lavric

University Politehnica of Bucharest, RO-011061, Polizu 1-7, Bucharest, Romania

ARTICLE INFO

Article history:

Received 9 June 2016

Received in revised form

1 August 2016

Accepted 11 August 2016

Available online 13 August 2016

Keywords:

4-Nitrophenol partition

Thermodynamic model

Complex interactions

Polar solvents

Associations

Dissociations

ABSTRACT

An enhanced partition model is proposed for the distribution of 4-nitrophenol between polar quasi-immiscible solvents (water and 1-octanol). Monitoring both phases over an extend wavelengths range (200–450 nm), the presence of 4-nitrophenol and 4-nitrophenolate species in the aqueous and organic layers was emphasized. A genetic algorithm has been used to minimize the sum of squared residuals model-experiment using the non-linear equations system model resulted from mass and charge balances. Thus, improved values for the thermodynamic constants associated to partition, dissociation and dimerization equilibria occurring in both phases were found: 1-octanol dissociation constant in the aqueous phase, $K_{Ow} = 3.2 \times 10^{-13} \text{ mol} \cdot \text{L}^{-1}$, 4-nitrophenol dissociation constant in aqueous phase, $K_{\Phi w} = 1.45 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$, water dissociation constant in the organic phase, $K_{wo} = 3.5 \times 10^{-16} \text{ mol} \cdot \text{L}^{-1}$, 1-octanol dissociation constant in the organic phase, $K_{Oo} = 1.1 \times 10^{-16} \text{ mol} \cdot \text{L}^{-1}$, 4-nitrophenol dissociation constant in organic phase, $K_{\Phi o} = 2.9 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1}$, 1-octanol dimerization constant in the organic phase, $K_{D_o} = 3 \times 10^{-9} \text{ L} \cdot \text{mol}^{-1}$ and 4-nitrophenol dimerization constant in organic phase, $K_{D_{\Phi}} = 1.4 \times 10^{-8} \text{ L} \cdot \text{mol}^{-1}$. Although the logarithms of calculated partition coefficients are rather similar to the values reported in the literature, in the 1.86–2.07 range, the collected experimental evidence demonstrates that the process had been oversimplified and the polar characteristics of the organic solvent had been neglected in the former studies. The enhanced partition model emphasized the nonlinear dependency of the partition coefficient upon the analyte concentrations.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

As early as 1872, Berthelot and Jungfleisch [1] had addressed systematically the distribution of a substrate between two immiscible liquids and pointed out the fact that the ratio of the substrate concentrations did not depend on the relative volumes of the solutions employed, being a constant, and referred to since as the partition coefficient, P . It was Nernst who in 1891 made the second significant contribution in the field, stressing that the partition coefficient is truly constant only if a single molecular species were considered partitioned between the two phases [2]. This approach led to treating partitioning as an equilibrium process, in which the tendency of a solute species to leave a solvent and move into another would be 'a measure of its activity in that solvent and

would be related to other commonly measured activity functions such as partial pressure, osmotic pressure, and chemical potential' [3].

Thus the 1-octanol - water partition coefficients started to be seen as embedding quantitative information concerning the lipophilic/hydrophilic nature of the partitioned substances, being the most popular descriptor for quantitative structure-activity relationship studies [4–6]. Apart from biochemical and drugs manufacturing industries, correct evaluation of partition coefficients is of uttermost importance in fundamental chemistry (for investigation of complex equilibria formation), chemical engineering (in connection to liquid-liquid separation, purification and carrier extraction), and food industry (for purification and extraction of caffeine, for example) [7].

Over the years, $\log P$ has been measured experimentally by many methods and techniques, like the shake-flask test [8], generator column (adapting a common HPLC column) [9], NMR [10], capillary electrophoresis [7,11] and counter-current chromatography [12].

^{*} Corresponding author. University Politehnica of Bucharest, 1-7 Gheorghe Polizu Street, Sector 1, RO-011061, Bucharest, Romania.

E-mail address: a_josceanu@chim.upb.ro (A.M. Josceanu).

The classical extraction approach has been widely used, leading to a handful of results [13]. A given amount of chemically pure compound is dissolved either in the aqueous or organic phase, which are put together and left to reach thermodynamic equilibrium under stirring, to enhance mass transfer such that its time constant to be several orders of magnitude lower than the contact time. Phases are then separated and the level of solute is determined in one or both phases by an appropriate technique (absorption spectrophotometry [8], chromatography [12], electrophoresis [11], etc.). Corrections should be applied if solutes display acidic or basic properties or are likely to self-associate. Usage of mutually saturated solvents is highly recommended, as the molar volume of wet 1-octanol is 126.6 cm³ and the water content is 1.64 M [14].

Several theoretical methods have also been developed to predict the partition coefficients, such as the fragment-based method of Rekker [15], the $C - \log P$ approach of Leo [16], ACD/log P [17] or atom-based methods like XLOGP [18], molecular lipophilicity potential, and related approaches [19,20], MS-WHIP topology descriptions [21], molecular property descriptions as Toulmin's $\Delta \log P$ method [22] or with the aid of Kovats retention indices [23]. The success of most additive–constitutive computation procedures based on molecular structures is highly dependent of the assessed accuracy of the corresponding databases [4,24,25].

The more complicated the structure of the third-party species, the more attention to the experimental and theoretical determination of the $\log P$ values should be given, with consideration of all possible secondary equilibria likely to occur in any of the two phases, especially when they are polar. Simpler molecules, such as 4-nitrophenol, did not receive more than an ionization correction [3] and the values obtained by fragment calculation and validated experimentally have not been reviewed for further adjustments. To the authors' best knowledge, the scientific community relies on the data reported by Hansch and Leo [3], validated through the shake-flask method with single wavelength spectrophotometric determination of solute levels. $\log P$ values for 4-nitrophenol have also been determined for water–chloroform [8], and water–cyclohexane [26] systems, measuring the solute amount mainly in the organic phase, and using mass balance equations to provide for the aqueous phase amount. Since concentration levels generally fell under 10⁻⁴ M, it was accepted that association in the organic phase was not favoured given the high dilution.

Investigation over a larger wavelengths domain, in the 250–450 nm region, points out that the repartition of 4-nitrophenol in the 1-octanol – water system has been significantly simplified (neglecting the polar nature of the former). Thus, a reinvestigation is necessary to provide a better insight into the elementary processes taking place in both polar phases. Careful monitoring of 4-nitrophenol and 4-nitrophenolate permits a better mass balance closure, with beneficial effects upon the accuracy of regressed thermodynamic equilibrium constants. This paper focuses on proposing a complex model for the distribution of 4-nitrophenol between water and 1-octanol, considering dissociation and association processes in both phases.

2. Experimental

Solid 4-nitrophenol, 5 × 10⁻⁴ – 10⁻³ M, was accurately weighed and contacted with different water: 1-octanol volume ratios for 24 h, in stoppered glass flasks, placed in an orbital shaker (ES–80, Grant Instruments), at 150 rpm, and 25 °C (298.15 K). This contact time was considered long enough for reaching thermodynamic equilibrium. A separatory funnel was used for water and 1-octanol separation. It has to be pointed out that a set of preliminary experiments was carried out using both centrifugation at 4000 rpm

and separation funnel for phase separation. Quantification of 4-nitrophenol content in each phase by spectrophotometry in the 200–450 nm region lead to the same result, regardless the separation procedure employed. Therefore, the standard experimental procedure included phase separation by separatory funnels. After separation, the amount of phenol in each phase was quantified by absorbance measurements using a Cary 50 (Varian) spectrophotometer in the 200–450 nm wavelength range. Variable path lengths were employed, as well as dilutions of certain organic samples to keep absorbance no higher than 0.9. Calibration curves for 4-nitrophenol in water saturated with 1-octanol were designed for 10⁻⁶ – 10⁻⁴ M solutions, and in 1-octanol saturated with water, for 10⁻⁵ – 5 × 10⁻⁴ M solutions. Calibration curves parameters were calculated by regression analysis applied to the experimental data collected in the 314–320 nm and 401–405 nm ranges for the aqueous solutions, as well as 310–316 nm and 392–397 nm ranges for the 1-octanol solutions of analyte.

The absorption spectra signalled the presence of both phenol and phenolate species (Fig. 1), so a separate calibration curve for 4-nitrophenolate in water saturated with 1-octanol was designed for a 10⁻⁶ – 10⁻⁴ M set of 4-nitrophenolate solutions prepared in 0.1 M LiOH. The corresponding parameters were calculated by regression analysis applied to data collected in the 401–405 nm range.

Solid lithium 4-nitrophenolate was obtained by solvent removal from a concentrated aqueous solution of lithium 4-nitrophenolate. After drying, it was used for preparing a set of solutions in 1-octanol saturated with water, in the 10⁻⁴ – 1.2 × 10⁻³ M concentration range. The actual concentration of the 4-nitrophenolate was accessible from the mass balance equation, as the absorption properties of 4-nitrophenol in the given solvent were already known. The actual concentrations of 4-nitrophenolate in the organic solutions varied between 4.3 × 10⁻⁵ and 1.9 × 10⁻⁴ M. The spectral domain used for determining the calibration curve parameters by regression was 392–397 nm.

Each partition experiment was run in triplicate. The reagents used in the experiment are presented in Table 1. Only 1-octanol was purified by distillation, the rest were used without further purification. Ultrapure water (18.2 MΩ/cm, Smart2Pure System from TKA, Germany) was used for calibration and extraction purposes. The volumetric glassware used for standard solutions preparation was class A.

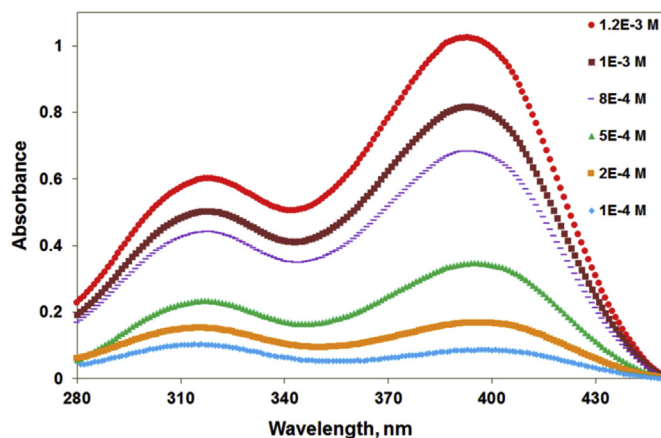


Fig. 1. Absorption spectra of 4-nitrophenol and 4-nitrophenolate in 1-octanol in the 0.1–1.2 × 10⁻³ M concentration range (total concentration) used for calibration (1 mm path length), at 298.15 K, and atmospheric pressure.

Download English Version:

<https://daneshyari.com/en/article/6619473>

Download Persian Version:

<https://daneshyari.com/article/6619473>

[Daneshyari.com](https://daneshyari.com)