

Polymer–water partition coefficients of extended range measured by using organic modifiers in the aqueous phase

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Abstract

A procedure for estimating equilibrium polymer–water partition coefficients over a broad range of solute hydrophobicity is presented and evaluated. The coefficients were calculated from the concentration change in the liquid phase and hydro-organic mixtures of varying proportions were used to extend the range. Three hydrophobic polymers (PP, PE, and EBA), two types of solvent (acetonitrile and alcohols) and 12 model solutes were used. The estimated polymer–water partition coefficients, $\log K_{pw}$, ranged from -0.5 to 8.5 . The coefficients correlated to other partitioning systems such as the calculated $\log P_{\text{octanol-water}}$ up to ~ 14 and the retention factor ($\log k_w$) in reversed-phase liquid chromatography.

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1. Introduction

For a polymer in direct contact with a solution, the distribution of low molar mass solutes between the phases is a fundamental interaction process. The equilibrium distribution of a compound between a solid and a liquid phase is determined by its differential solubility in the two phases. The corresponding polymer–solution partition coefficient is therefore an important basic measure that is used in numerous studies, for example, interactions and sorption kinetics in polymer–solvent systems [1]. Depending on the value of the partition coefficient for each species in the system, the interaction upon equilibration will range from leaching of components from the polymeric material (desorption) to binding of components from the solution by the material (sorption). Low molar mass additives, such as plasticizers or antioxidants, are known to leach into the environment, causing health issues or

shortening of the expected lifetime of the polymer, at a rate that depends on the partitioning to the surrounding material. Moreover, in the packaging of pharmaceuticals and foods, these processes could impair the quality and safety of the product. In a review article Tehrani and Desobry [2] summarized the theories and factors influencing polymer partitioning, focusing on food packaging systems. They discussed the influence of temperature, the chemical structure and size of the migrant, and the pH and other characteristics of the liquid phase.

The sorption–desorption balance may also be utilized in many ways. Polymers can be used to release a controlled amount in drug delivery systems [3]. Another example is in studies of complex systems such as the gastrointestinal absorption of drugs, where silicone sheets acted as a partitioning receptor phase [4]. Polymer sorbents are also used as stationary phases in chromatography and in analytical sample preparation to extract and concentrate hydrophobic analytes from a liquid phase. In a recent example, phthalate esters released into water by leaching from food contact polymers were analyzed after enrichment by microdialysis on a polysulfone hollow fiber [5]. Meluch and Lloyd [6] compared partition

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coefficients obtained by liquid chromatography (LC) to those from equilibrium partition experiments for various alcohols in a water–cellulose acetate system. They used cellulose acetate powder as the stationary phase and injected the alcohols in water as the mobile phase. Equilibrium was, however, not attained in LC due to the kinetics of diffusion into the core of the cellulose particles, although the data were qualitatively useful.

Polymer–solution systems are being used as models for other partitioning systems and *vice versa*. Mostly $\log P$, the distribution coefficient of neutral compounds between two immiscible liquids, is applicable. A novel way of estimating $\log P_{ow}$ (octanol–water) for highly lipophilic solutes from the binding into PDMS discs has been proposed [7]. The fiber–water distribution in SPME is also correlated to $\log P_{ow}$ [8]. Likewise, the partitioning of solutes from an aqueous solution to polypropylene (PP) and polyethylene (PE) has been found to correlate closely to their hexane–water partition coefficients [9], while the octanol–water partition coefficient has been used in other studies and polymers [10,11]. The $\log P_{ow}$ was found to be applicable to plasticized polyvinylchloride (PVC), for example, although for PE or PP, with no or very low hydrogen bonding activity, a combination of several $\log P_s$, such as $\log P_{ow}$ and $\log P_{hw}$ (hexane–water), was found to be more applicable [12]. Liquid chromatography, using different types of stationary phases, is often used for an automated estimation $\log P$. Jenke et al. [13] used a reversed-phase LC silica C_8 -system for the determination of $\log P_{ow}$ in a study of container interactions. In a comparison between a silanol-deactivated amide C_{16} and a polymer-based octadecylpolyvinyl (ODP) stationary phase, the silica-based column showed the best correlation to $\log P_{ow}$ [14]. For $\log P_{aw}$ (alkane–water), a polymer-based column has been shown to provide quite a good estimation [15]. A polymethacrylate gel based column with octadecyl groups, used to extend the pH range, has proven useful for lipophilicity determinations [16]. $\log P_{ow}$ may be experimentally determined or calculated from the structure of the solute by using suitable software. Although the calculated value is an approximation, it is convenient to use and is applicable to highly hydrophobic solutes, for which an experimental measurement is very difficult or practically impossible.

The equilibrium polymer–solution partition coefficient depends on all three parts in the system – the solute, the polymer, and the composition of the liquid phase – and is defined as the ratio of the concentration of the solute in the polymer to that in the solution:

$$K = c_{\text{polymer}}/c_{\text{solution}} = c_p/c_s \quad (1)$$

Gavara et al. [17] determined the partitioning of organic compounds in polystyrene–water systems and compared three experimental techniques. They used size exclusion chromatography and dynamic thermal stripping thermal desorption (DTS-TD) to determine the equilibrium concentration in the polymer, and gas chromatography was used for determination of the solute concentration in the water phase. The solution was pre-concentrated by an extraction step to accurately

quantify the solute concentration since the high affinity for the polymer resulted in a very low equilibrium concentration in the solution. This example illustrates some of the practical obstacles associated with high partition coefficients. A solute's partition coefficient can be determined from its concentration in only one of the phases, provided the total amount of solute available in the system and the volume/mass of the two phases are known. Due to the unavoidable extraction step when quantifying the amount of solute in the polymer it is more convenient to use its concentration in the liquid phase, but the sensitivity of the analytical procedure becomes the limiting factor for high partition coefficients. For polymer–water systems, the use of binary hydro-organic solvent mixtures over water alone makes it possible to control and moderate the partition ratio in order to facilitate the quantitation. A series of water solutions containing 0–100% of ethanol was used in a study of flavor desorption from low density PE and polyethylene terephthalate (PET) packaging films [18]. Jenke [19] showed that there is a linear correlation between the polarity of the solvent and the equilibrium binding constant for a series of solutes in contact with PVC and a multicomponent polyolefin film. In subsequent studies by the same author, binary mixtures of ethanol–water were used to model the polarity of pharmaceutical formulations in the assessment of container/content interactions [20,21].

This principle is used when regulating the retention in reversed-phase liquid chromatography (RP-LC) by the admixture of an organic modifier to the aqueous mobile phase. The chromatographic retention is due to the partitioning of the analyte between the stationary and mobile phases. The logarithm of an analyte's retention factor, $\log k$, is ideally linearly related to the fraction of organic modifier in the mobile phase (φ):

$$\log k = \log k_w + S\varphi \quad (2)$$

The intercept, $\log k_w$, corresponds to the retention when pure water is used as the mobile phase and is determined indirectly at $\varphi \neq 0$, since most compounds will be completely retarded using 100% water as mobile phase. The S -value depends on the identity of the organic modifier and is an approximate descriptor of solvent strength [22]. Since, the stationary phase is affected by changes in the composition of the binary mobile phase there are limitations to this linear model unless the composition range (φ) is restricted. Another drawback is that the $\log k_w$ is usually not independent on the identity of the organic modifier due to interactions with the stationary phase. However, in a partitioning system where the solid phase is less affected by the identity and composition of the liquid phase, then Eq. (2) becomes applicable. Thus, provided this prerequisite is met, it would be possible to use this model to measure the polymer–water partition coefficient over an extended range in solute hydrophobicity.

Here, the aim is to develop a fast and convenient procedure for estimating the polymer–water partition coefficient that works over a broad range of solute lipophilicity. Hydro-organic mixtures are used over pure water in order to increase

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