



An analytical solution to the idealized batch pervaporation experiment: A way to determine the diffusion and partition coefficients



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ABSTRACT

The physicochemical basic laws and their suitable mathematical formulations form a frame of the batch pervaporation process, i.e. the cycled process of removing small traces of volatile impurities from large amounts of a volatile solvent, is described and analyzed in detail.

The generic nature of the process, i.e. its exclusively transient behaviour is described as an IBV (initial boundary value) problem with a feed side boundary condition dependent on time. The long time asymptotics is investigated to determine the partition and diffusion coefficients of the trace.

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1. Introduction

Pervaporation is one of the membrane separation techniques, especially useful for removing small traces from the liquid mixtures, for example small amount of organic components from contaminated water or in the enhancement of azeotropic mixture separation quality [1–4]. The central idea of pervaporation is based on selective membrane as an essential part of the set-up that lets the trace to pass while the main component of a mixture is passive.

In this paper we would like to critically discuss the physicochemical fundamentals of pervaporation and mathematical formulation of two frequent problems starting from ideally selective membrane. This simplified approach will enable us to show, in a clear way, where the problem is.

Let us start with a schematic visualization of the batch pervaporation setup [2,4–7]. The setup is shown in Fig. 1. It is quite evident from the scheme that during the process the concentration of trace in the feed becomes smaller and smaller. Consequently, the driving force for the trace diffusion through selective membrane decreases with time. Let us check, step by step, how it goes.

Suppose that the feed container has a volume V , the membrane has a surface A , and the initial trace concentration (expressed as a mass concentration) is equal to c_T^0 . The trace concentration

depends on time and it is a decreasing function:

$$c_T(t) = c_T^0 - \frac{A}{V} \int_0^t J(0, \tau) d\tau \quad (1)$$

where $J(0, t)$ stands for the flux through the membrane on the feed side, which can also be written in differential form, which is more suitable for numerical evaluation:

$$\frac{dc_T(t)}{dt} = -\frac{A}{V} J(0, t) \quad (2)$$

The trace undergoes a partition with the feed side of the membrane according to some proportionality coefficient. To evaluate the partition, we can make use of Henry's and Raoult's laws [8].

To start with, let us consider that each liquid contains molecules, which energy makes them ready to escape from the bulk of the liquid. We can estimate the effective pressure of such escaping molecules by considering the equilibrium of their vapour with the liquid:

$$p_T = x_T(t)p_T^0 \quad (3)$$

where $x_T(t)$ is the molar fraction of the trace and p_T^0 is the vapour pressure of a pure component. The vaporized molecules partition with the membrane giving the boundary condition for a concentration in the membrane:

$$c(0, t) = S_T p_T(t) \quad (4)$$

where S_T is a partition (solubility) coefficient [9].

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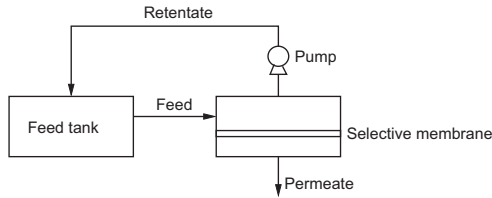


Fig. 1. A schematic representation of a batch pervaporation set-up.

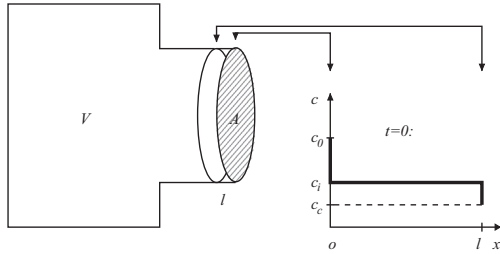


Fig. 2. The experimental setup that corresponds to equation set (8)–(12).

By the assumption of c_T to be very small (the trace!), one can use Raoult's and Henry's laws with constant coefficients, i.e. p_T^0 and S_T , respectively. This allows us to calculate $x_T(t)$:

$$x_T(t) = \frac{c(0, t)}{S_T p_T^0} \quad (5)$$

which can be converted to the concentration $c_T(t)$ by

$$\frac{c_T(t) \bar{M}}{\bar{c} M_T} = x_T(t) \quad (6)$$

which, after approximating the average molar mass of the system \bar{M} by the molar mass of the solvent M_S , and the average concentration \bar{c} by the solvent concentration c_S , and a small rearrangement, results in

$$c_T(t) \approx x_T(t) c_S \frac{M_T}{M_S} = c_S \frac{M_T}{M_S S_T p_T^0} c(0, t) \quad (7)$$

where M_T is the trace's molar mass.

In the following, after presenting an analytical solution to the bath pervaporation problem, we would like to assess the proportionality coefficient between $c_T(t)$ and $c(0, t)$, and disassociate it from the diffusion coefficient.

2. Mathematical formulation and its critical discussion

Assuming that the membrane is ideally permselective, i.e. only the trace is transported and that $x_T \ll 1$ which implies $c_T \sim 0$, so we can treat the feed volume V and diffusion coefficient D as a constant (the latter is not always true, as shown for example in [10]). In such ideal situation we can write (Fig. 2)

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (8)$$

$$c(x, 0) = c_i \quad (9)$$

$$\frac{dc(0, t)}{dt} = -\frac{S_T M_S p_T^0 A}{V M_T c_S} J^a(0, t) = -\frac{H}{l} J^a(0, t) \quad (10)$$

$$c(0, 0) = c_0 = \frac{M_S S_T p_T^0}{M_T c_S} c_T^0 \quad (11)$$

$$c(l, t) = c_c \quad (12)$$

Let us discuss the above set of equations one by one. Condition (9) says about two options: $c(x, 0) = 0$ reflex the situation of an empty membrane, i.e. evacuated by the vacuum pump. $c(x, 0) = c_i$ mimics the situation in which this is not possible (chitosan membranes which need water to be stable). Conditions (10) and (11) reflect Eqs. (2), where we change the variable from c_T^0 to c_0 , by introducing a constant $H = l S_T M_S p_T^0 A / V M_T c_S = (l A / V) c_0 / c_T^0$ to simplify the form of relation (based on (7)) and to shape the parameters to fit the literature model. We can do this because c_T^0 and c_0 are interrelated by the partition phenomenon. It describes the very nature of the process, i.e. that certain amount of feed circulates in a closed system and undergoes purification by the permselective transport through a membrane.

3. Results and discussion

3.1. The full solution

The prototype of a full solution of the equation set (8)–(12) can be found in the heat conduction literature and in the literature related to the diffusion in a closed container [11,12]:

$$c(x, t) = c_c + 2 \sum_{n=0}^{\infty} \frac{[(c_i - c_c)(H^2 + Q_n^2) \sin Q_n + (c_0 - c_i) H Q_n] \sin \frac{Q_n(l-x)}{l}}{(H + H^2 + Q_n^2) Q_n \sin Q_n} \times e^{-D Q_n^2 t / l^2} \quad (13)$$

where the parameter Q_n is a solution of the transcendental equation:

$$Q_n \tan Q_n = H \quad (14)$$

with n numerating the subsequent positive solutions: $n=0$ for the lowest value of Q , the Q_0 which is of crucial importance for this work (Fig. 3). A derivation of this result (for $\hat{x} = l - x$) is shown in the appendix of [11]. In short, this transcendental equation results from the requirement to satisfy condition (10) by the expansion of the form

$$c(\hat{x}, t) = c_c + \sum_{n=0}^{\infty} \left[A_n \sin \left(\frac{Q_n \hat{x}}{l} \right) + B_n \cos \left(\frac{Q_n \hat{x}}{l} \right) \right] \exp \left(-\frac{D Q_n^2 t}{l^2} \right) \quad (15)$$

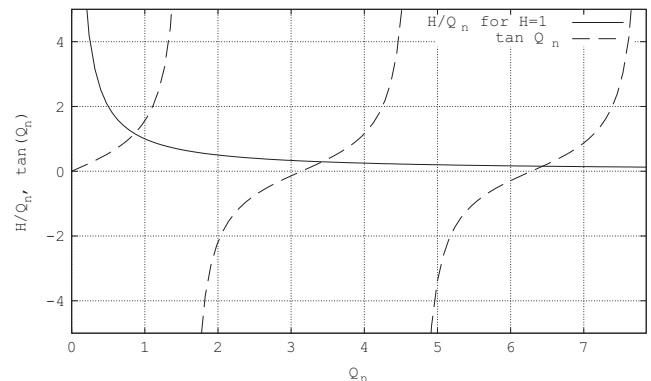


Fig. 3. The points of intersection of $\tan Q_n$ and H/Q_n solve the transcendental equation $Q_n \tan Q_n = H$.

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