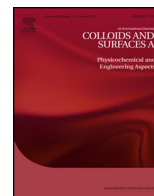




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Modeling of osmotic kinetics in aqueous solutions, based on experimental data

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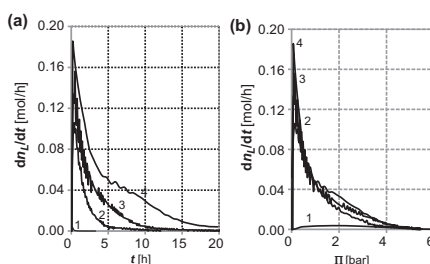
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HIGHLIGHTS

- New experimental approach of limited volume variation is developed and applied.
- Osmotic kinetics is compared at two regimes: constant and variable solution volume.
- Kinetic dependences reveal divergences at constant and varied solution volume.
- Osmotic rates exhibit maxima as a function of time and pressure.
- Hypothesis of a polarization effect in the near-membrane space is put forward.

GRAPHICAL ABSTRACT



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ABSTRACT

Osmotic kinetics in aqueous glucose solutions was investigated at two distinct experimental regimes: of constant solution volume and of controlled volume variation. Although osmotic equilibrium is considered to be well understood from thermodynamic viewpoint and does not pose serious ambiguities, the dynamic aspects of the process often exhibit new and even surprising effects, which are difficult to explain within the frames of the traditional kinetic models. Such a non-trivial effect is the appearance of maxima in the rates of solvent transfer, as derived from the obtained kinetic dependence 'osmotic pressure vs. time'. The attempt to interpret such maxima brought the hypothesis of a polarization effect in the near-membrane space: local dilution of solution, due to the influx of solvent, which in its turn raises a diffusion flux from the bulk. Obviously, at the end (at equilibrium) the concentration should be again homogeneously distributed, after passing through a minimum, which could be the cause for the osmotic rate maxima.

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1. Introduction

Osmosis is the spontaneous flow of solvent through a semipermeable membrane from a phase of a higher chemical potential of

the solvent to a phase of lower chemical potential. The flow continues until the chemical potentials become equal on both sides of the membrane. In case when additional energy (e.g. gravitational, electrostatic, etc.) is involved, the equilibrium is determined by the respective generalized chemical potential. The concentration difference between the two solutions causes solvent transport and creates pressure difference across the membrane (osmotic pressure). This solvent transport through the membrane is in principle

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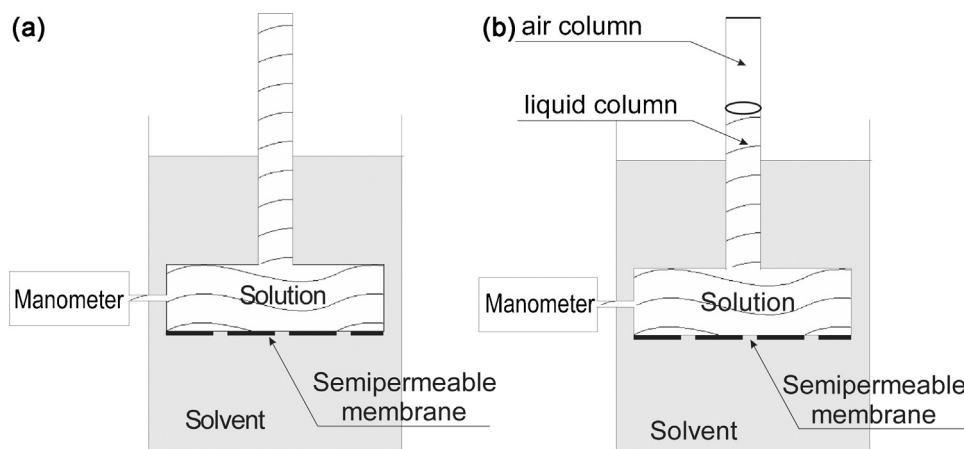


Fig. 1. Schematic of the osmotic cell at the two experimental regimes: (a) Constant solution volume; (b) Variable solution volume.

a hydrodynamic process (momentum transport). In cases where the membrane pores diameter is much smaller than their length (“thick” membranes), the osmotic flow is governed by the well known Poiseuille law.

Equilibrium studies of osmosis, whether theoretical or experimental, predominate in the literature, while the kinetic aspects of the process, which are of real interest for natural (biological) structures, as e.g. the living cells and many technological applications, have drawn relatively less attention through the years [1–4]. Few phenomena are so well understood thermodynamically, or so ill understood kinetically, as the osmotic flow of a solvent through a semipermeable membrane [4]. Osmotic equilibrium is considered to be well understood from thermodynamic viewpoint and does not pose serious ambiguities. In contrast, the dynamic aspects of the process frequently exhibit new and even surprising effects, which are difficult to explain within the frames of the traditional kinetic models.

Osmosis is essential in biological systems. The exchange of matter with the medium at cellular level takes place in such a mode. Considering the characteristics of the cellular structure, the osmotic transfer may acquire complexity. More prominent are the following cases:

- (i) The pore diameter is comparable to the size of the solvent species. Then the solvent transfer does not obey the Poiseuille law and claims special modeling (e.g. [2–4]);
- (ii) The pore diameter is comparable to the size of the solute species. This is typical for the process of extraction, where intracellular substances are first dissolved into the squeezing in solvent and then leave the cell with the outflow of solution [5–7].
- (iii) Osmosis in the cells occurs in confined volumes, which may also impose its specificity [8].

The kinetic studies reported in the literature chiefly treat the above problems, concerning the permeability of the membrane, in particular the case of coupled solvent-solute transport [7], generalization of the Fick and Poiseuille equations for pores of molecular dimensions [2–4], etc. Classical macro-kinetic data about aspects of the process such as the rate of pressure rise in the solution chamber or the rate of solvent transfer are, in fact, absent.

The aim of the present investigation has been to examine the specific features of the osmotic process in aqueous solutions under dynamic conditions, applying two different experimental regimes: of constant and variable solution volume. Further aim of the work is to model the process on the basis of the experimental data.

2. Experimental method and data

Polyamide composite type semipermeable membranes for reverse osmosis (RO-KOCH membranes) were used. They are specified as able to reject >99% of small molecules, like those of the chosen here glucose, as well e.g. the NaCl ions. The membranes were used within the prescribed ranges: pH 4–11; temperature <50 °C.

We have conducted the experiments with a custom-made membrane osmometer [9,10]. It consists of two cylindrical plastic shells: for solvent and solution, respectively. Membrane of 5.0 cm diameter is sealed between the shells and is supported against deformations by two additional perforated Plexiglas disks on either side. The active operative area of the membrane (the integral surface of holes on the perforated discs) is ca. 5 cm². The osmometer employed in our investigation of equilibrium osmotic pressure had solution compartment of constant volume [9]. The following kinetic study required additional refinement and we applied our novel modification with limited variation of the solution volume [10]. A constant volume osmotic regime is realized in a chamber that is completely filled with solution, while at the regime of variable volume, room is also left for a controlled amount of gas (air).

Schematic of the osmotic cell is presented in Fig. 1. Graduated, 1.3 m long, transparent plastic tubing of 2 mm radius was fixed onto the solution chamber to provide control over the liquid and gas amount in this compartment at variable volume. With initial capacity of the solution compartment of 60 cm³, the attached tube provided variable additional volume of ca. 16 cm³, that is, a possibility of volume change by up to some 25%. The ultimate solution concentration was determined by means of the amount of solvent transferred through the membrane.

Next we shall present the key experimental data, which induced the current study. It may well be acknowledged that Fig. 2 contains the entire dynamic information about the osmotic process, projected to be analyzed here. Glucose, a biologically active substance used as a reference solute in osmotic studies, was chosen for the current investigation. High purity 5% glucose solutions, produce of B. Braun Melsungen AG, Germany were used as received in our experiments. All experimental runs are conducted at constant temperature (22 °C), and the same initial concentration of solute ($c = 0.278$ mol/L).

Fig. 2 is a presentation of the ‘osmotic pressure Π vs. time t ’ dependences, as obtained for the two different experimental regimes: of constant solution volume (curve 1) and variable solution volume (curves 2–4). The obtained dependences exhibit similar pattern, so that the main difference is in their respective

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