Calibration of membrane inlet mass spectrometric measurements of dissolved gases: Differences in the responses of polymer and nano-composite membranes to variations in ionic strength

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ABSTRACT

This work examines the transmission behavior of aqueous dissolved methane, nitrogen, argon and carbon dioxide through two types of membranes: a polysiloxane nano-composite (PNC) membrane and a conventional polydimethylsiloxane (PDMS) membrane. Transmission properties at 30 °C were examined by membrane introduction mass spectrometry (MIMS) at nearly constant gas partial pressures in NaCl solutions over a range of ionic strength (0–1 molal). Gas flow rates were examined as a function of dissolved gas concentrations using the Setschenow equation. Although MIMS measurements with PDMS and PNC membranes produced signal responses that were directly proportional to aqueous dissolved gas concentrations, the proportionalities varied with ionic strength and were distinctly different for the two types of membranes. With the exception of carbon dioxide, the PNC membrane had membrane salting coefficients quite similar to Setschenow coefficients reported for gases in aqueous solution. In contrast, the PDMS membrane had membrane salting coefficients that were generally smaller than the corresponding Setschenow gas coefficient for each gas. Differences between Setschenow coefficients and membrane salting coefficients lead to MIMS calibrations (gas-flow vs. gas-concentration proportionalities) that vary with ionic strength. Accordingly, gas-flow vs. gas-concentration relationships for MIMS measurements with PDMS membranes are significantly dependent on ionic strength. In contrast, for PNC membranes, flow vs. concentration relationships are independent (argon, methane, nitrogen) or weakly dependent (CO_2) on ionic strength. Comparisons of gas Setschenow and membrane salting coefficients can be used to quantitatively describe the dependence of membrane gas-flow on gas-concentrations and ionic strength for both PDMS and PNC membranes.

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1. Introduction

Measurement of gas concentrations in aqueous solution is of great importance in a wide variety of scientific, regulatory and commercial applications [1–5]. Detection and quantification of dissolved gases often involves the use of membranes in conjunction with colorimetric pH indicator techniques, polarography or mass spectrometry [1,2,6,7]. Colorimetric and polarographic techniques generally allow measurement of a single gas in solution [6,7], while mass spectrometry facilitates measurements of multiple gaseous components simultaneously [1,2]. As a second important distinction between mass spectrometric measurements of gas concentrations and other membrane-based techniques, membrane introduction mass spectrometry (MIMS) involves measurement of

flow rates [8], while other procedures are based on chemical equilibrations. As a result, MIMS can not only provide comprehensive measurements of a variety of gases in solution but can also make measurements on much shorter time scales than are required by equilibrium techniques.

The responses of MIMS systems are strongly regulated by membrane permeability properties. The permeability of polydimethylsiloxane (PDMS), a frequently preferred membrane material, is strongly influenced by gas partitioning between the solution phase and the vapor phase through a process known as pervaporation. This process can be used to describe transmission properties of dissolved gases through the membrane interface into the detector. Ordinarily, MIMS measurements are performed at atmospheric pressure, but the substantial utility of this technique has also led to its in situ employment at hydrostatic pressures greater than one atmosphere [9–13]. At higher hydrostatic pressures, conventional PDMS membranes have been reported to demonstrate variable permeability properties [14,15].

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Miranda et al. [16] recently described the gas transmission characteristics of polysiloxane nano-composite (PNC) membranes that were coupled to the inlet system of a mass spectrometer. The gas transmission properties of PNC membranes were compared to those of a conventional PDMS membrane over a range of hydrostatic pressures. The PDMS membrane exhibited compression of its siloxane matrix when hydrostatic pressure was increased, and exhibited hysteresis when hydrostatic pressure was subsequently decreased. Thus the permeability properties of the PDMS membrane are influenced by hydrostatic pressure in a manner that presents substantial challenges to quantitative calibration. In contrast, the transmission properties of the PNC membranes constructed by Miranda et al. [16] demonstrated little if any response to changes in hydrostatic pressure.

Having previously shown that PNC membranes are much less susceptible to hydrostatic pressure-induced variation in permeation properties than PDMS membranes, this work examines the comparative gas-transmission properties of PNC membranes and PDMS membranes over an environmentally-relevant range of ionic strengths. Using gas mixtures with constant compositions, gas concentrations in equilibrated solutions were varied (i.e. decreased) with increasing NaCl concentration (ionic strength) while gas partial pressures were essentially constant. This investigation shows that variations in ionic strength exert much smaller influences on the permeation of gases through PNC membranes than conventional PDMS membranes. Additionally, it is shown that the influence on ionic strength on MIMS calibrations (gas-flow vs. gas-concentration) can be well-described in terms of differences between membrane salting coefficients and Setschenow coefficients for both PDMS and PNC membranes.

2. Theory

2.1. Gas solubility theory

The concentration of gas ($C_{(aq)}$) in an aqueous solution when a gas phase and solution phase are in equilibrium can be described using Henry's Law [17]

$$C_{(aq)} = \beta P_p \tag{1}$$

where β is the solubility constant for a gas in an aqueous solution and P_p is the partial pressure of a gas in equilibrium with the solution. Gas concentrations in solution can be expressed in terms of gas activity coefficients (γ_G) via the following relationship: $C_{(aq)} = a_G / \gamma_G$, where a_G is the activity of a gas in solution. The concentrations (or solubility) of gases in aqueous solution are decreased by addition of salts (i.e. the salting-out effect) as γ_G increases with salt content. The relevant measure of comparative concentrations of a particular gas in solutions of variable salt content is the ionic strength, I [18]. At constant temperature and partial pressure, the comparative solubility of a gas over a range of ionic strength can be well described using the Setschenow equation [19,20]:

$$\ln(\beta^\circ / \beta_s) = \ln(\gamma_{G,s}) = k_s I \tag{2}$$

where β° and β_s are solubility coefficients for a gas in pure water ($I=0$) and a solution with ionic strength (I), $\gamma_{G,s}$ is the activity coefficient of a gas in a solution with ionic strength and k_s is the salting-out coefficient for a given gas.

2.2. Membrane introduction mass spectrometry (MIMS) theory

Membranes (e.g. PDMS and PNC) act as interfaces between sample solutions and the vacuum of a mass spectrometer. Transport through the membrane (as a pervaporation process) is induced by maintaining the vapor pressure on the permeate side

at a lower vapor pressure than in the feed liquid. The pervaporation process involves a sequence of three steps: (i) selective sorption of analyte(s) into the membrane on the feed side, (ii) diffusion of the analyte(s) through the membrane, and (iii) desorption of the analyte(s) into a vapor phase on the permeate side of the membrane [21]. The solution–diffusion model assumes that, at the solution/membrane interface the activity of an analyte in the feed liquid is equal to the activity of the analyte in the membrane [22]. The activity (a_m) of an analyte in the membrane on the feed (solution) side of the membrane is given as: $a_m = \gamma_m C_m$, where γ_m and C_m are the activity coefficient and the concentration of an analyte in the membrane at the solution/membrane interface. Under steady-state conditions, the ion current (Φ) measured by the mass spectrometer is directly proportional to the flow (F) of an analyte across a membrane and can be described by the following equations [23–33]:

$$F = \Phi \omega \tag{3a}$$

$$F = AD(a_m / L) \tag{3b}$$

where ω is a proportionality constant, A is the membrane surface area, D is the analyte diffusion coefficient, and L is the membrane thickness.

3. Experimental procedures

The PDMS membrane used in this work was of conventional design, with surface area and membrane thickness comparable to those of PDMS membranes reported by other research groups [23,24,34,35]. In contrast, the PNC membranes used in this work were fabricated using novel techniques.

Synthesis and characterization of polysiloxane nano-composite (PNC) membranes are described in Miranda et al. [16]. An overview of the process is given as follows: an anodic aluminum oxide (AAO) membrane was mounted on a stainless steel frit and secured on a membrane module with vacuum epoxy. A thin polysiloxane film was mechanically coated on the surface of the AAO using a room-temperature-vulcanizing silicon rubber. Two membranes were created in this manner and mounted in series on a custom-made manifold membrane module. The AAO membranes were 60 μm thick and had pores with an average diameter of 200 nm. Polysiloxane films were uniformly deposited across the upper surface of the AAO membranes and, on average, were 11 μm thick. The cumulative area of the PNC membranes was ~6.2 mm².

The PDMS membrane (Specialty Manufacturing Inc.) used in this work was 127 μm thick and had a total area of 2.8 cm². The PDMS membrane was mounted on a custom-made membrane module (Fig. 1).

Mass spectrometry measurements were conducted using an experimental configuration similar to that described in Miranda et al. [16]. The PNC and PDMS membrane modules were connected individually to a quadrupole mass spectrometer (Inficon, Transpector 2.0 Gas Analyzer System) via a Swagelok fitting. Solutions were pumped through the membrane modules using a peristaltic pump. The peristaltic pump was placed downstream of the membrane module. MIMS measurements were made using a Faraday cup detector.

Four solutions, each in a (500 ml) volumetric flask, were placed in a constant temperature water bath (30 °C). One set of solutions, deionized (DI) water and a sodium chloride solution, were simultaneously equilibrated at atmospheric pressure with a gas mixture (Airgas certified) while the other set (of similar solution composition) were simultaneously equilibrated at atmospheric pressure with a baseline gas. Measurements were obtained using gas mixtures containing methane (CH_4), argon (Ar), carbon dioxide