Kinetics of Diffusion of Water and Dimethylmethylphosphonate Through Poly(dimethylsiloxane) Membrane Using Coated Quartz Piezoelectric Sensor

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ABSTRACT: The mass sensing principle of quartz crystal has successfully been employed to study the diffusion of dimethylmethylphosphonate (DMMP) and water through a poly(dimethylsiloxane) (PDMS) membrane. For this study a new permeation cell has been fabricated which houses a Cu(II) butyrate ethylenediamine-coated quartz crystal sensor. This development was motivated by the desire to measure the diffusion coefficients rapidly, precisely, and at different temperatures. Temperature dependence diffusion coefficients of DMMP and water are also evaluated using the same cell, which enables calculation of the activation energies for the diffusion process. From the diffusion and solubility data permeability coefficients of DMMP and water have been calculated. It is observed that PDMS membrane offers a selectivity for DMMP over water roughly by 13 : 1 (i.e., $P_{DMMP}/P_{water} > 13$). © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1789–1794, 1997

Key words: piezoelectric sensor; diffusion cell; PDMS membrane; diffusion; kinetics of diffusion

INTRODUCTION

Poly(dimethylsiloxane) (PDMS) is a known hydrophobic material. It has a tendency to discourage the passage of water molecules, while at the same time allowing the passage of a wide range of larger organic molecules.[1] PDMS membrane not only behaves as a sieve, but also behaves as a true chemical separator which depends on the nature of the permeating molecules. It is for this reason that PDMS membrane is used in different environmental analytical detection inlet systems, e.g., portable G.C., portable MS, ion mobility mass spectrometry, etc.[2] It is therefore worthwhile to investigate in detail the diffusion and kinetics of

diffusion of different permeants through PDMS membranes.

The time-lag method, in which the permeate gas or vapor accumulates in a preevacuated downstream volume, is still widely used for the determination of diffusion coefficients.[3–5] This method assumes that the diffusion coefficient is constant throughout the permeation process from initiation to steady-state permeation. In a permeation process where the diffusion coefficient is not constant, use of the time-lag method can lead to significant error.[6] It is reported that this error can be avoided by first differentiating the integrated output signal in order to obtain the true permeation resistant.[7] In practice the use of the above technique is rare. Basically, there are a number of reasons to doubt the reliability of the above differentiating method.[7] It has also been thought that the time-lag method may be more useful for
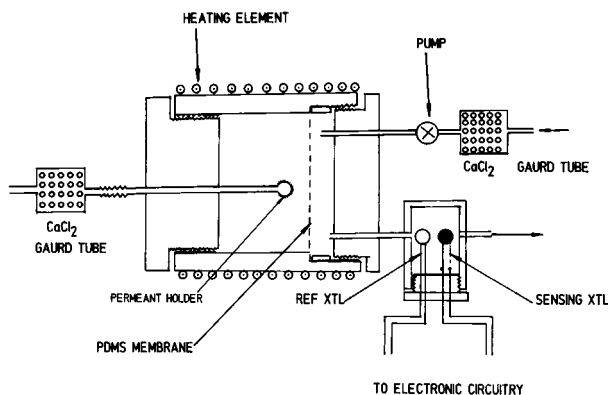

Figure 1 Cross-sectional sketch of the permeation/diffusion cell.

determining the diffusion coefficients by using a rapid sensor. In that search, FTIR–ATR has been employed by a group of workers.[8,9] More recently, we have also reported the study of diffusion of different chemical pollutants through different polymeric membranes by the FTIR–ATR method.[10,11] However, this method suffers from a number of limitations; the instrument is costly and the setup is cumbersome to some extent. The method also has some advantages; e.g., it is a universal detector and the diffusion of more than one permeant can be studied simultaneously if the different permeants have well-defined IR stretching frequencies.

Coated piezoelectric quartz crystals have been widely used as selective and sensitive sensors for detection of various gases and organophosphorus (OP) compounds.[12,13] It has also been reported that modification of the crystal surface with suitable coating materials and enzymes that will reversibly bind a particular gaseous substrate can provide enhanced specificity.[14–16] In most of the studies change in frequency of a single crystal oscillator had been monitored and the deposited mass on the crystal is a function of change of frequency, which can be calculated according to the Sauerbrey equation.[17,18] More recently, use of a dual crystal oscillator followed by a mixture and filter to select the difference frequency had also been reported for similar studies.[19]

We planned to utilize the quartz piezoelectric crystal as a sensor for detection of different toxic OP compounds like sarin and soman. In that search we found Cu(II)butyrate ethylenediamine is a specific coating material.[20] Although the coating material is specific to the OP compounds, it is observed that water vapor and ammonia interfere with the coating material and result in a false

signal. To avoid this we thought to use PDMS membrane as a separator membrane in the environmental sampling inlet. To fulfill this goal, the diffusion of dimethylmethylphosphonate (DMMP; simulant OP compound) and water was studied in a prefabricated diffusion cell; details of this have already been published in our previous article.[21] The aim of the present article is to study the diffusion and kinetics of diffusion of DMMP and water through a PDMS membrane using a modified diffusion cell that has the facility to put the membrane at various controlled temperatures while sensing and reference crystals are kept at ambient temperature.

EXPERIMENTAL

Preparation of Cu(II)butyrate ethylenediamine

The compound was prepared by reacting freshly prepared copper butyrate with freshly distilled and dehydrated 1,2-ethylenediamine (Fluka, Switzerland) (1 : 1) in dehydrated methanol (SD, India). The dark blue compound so obtained was characterized by copper estimation, elemental analysis, and IR analysis.

Preparation of PDMS membrane

PDMS membranes of different thickness were prepared from commercially available silicone rubber (semicompounded stock from Anabond Silicones, India, SILURUB, NPC-40 U). Silicone rubber was mixed with 1 wt % of dicumyl peroxide in a two-roll rubber mixing mill and heat-cured in a hydraulic press at 170°C for 8 min [Tensile strength of the cure sheet was measured to be 600 psi and elongation at break point is 227%, hardness = 47 (Shore "A")]. DMMP (Fluka, Switzerland) was distilled prior to use.

Permeation/Diffusion Cell Assembly

A jacketed cylindrical diffusion cell was fabricated from thick (10 mm) brass (height 40 mm, internal diameter 40 mm). The temperature of the cell was controlled to an accuracy of ±1°C with the help of a temperature control circuit. The cell can be closed by two lids which can be screwed to the main body. The PDMS membrane was placed in a slot below the right-hand lid of the cell. The lid is connected to the crystal housing containing both reference and sensing crystal and circulating

Table I   Sorption Uptake Responses of the Coated Crystal in Terms of Frequency Change (Hz) with Time (s)

ΔF (Hz)	Time (s)					
	100°C		120°C		150°C	
	DMMP	Water	DMMP	Water	DMMP	Water
50	108	126	98	92	43	46
100	118	148	103	112	53	56
150	—	163	—	124	—	64
200	136	179	113	136	70	69
250	—	195	—	148	—	72
300	152	210	123	162	83	75
350	—	226	—	174	—	78
400	168	242	133	186	89	81
450	—	258	—	200	—	84
500	181	272	140	212	92	87
550	—	288	—	224	—	90
600	185	304	144	237	95	93
650	—	320	—	250	—	96
700	189	—	148	—	98	99
750	—	—	—	—	—	102
800	193	—	153	—	100	105
850	—	—	—	—	—	108
900	189	—	156	—	103	—
1100	206	—	164	—	109	—
1300	213	—	172	—	114	—
1500	221	—	180	—	120	—
1700	229	—	188	—	125	—
1900	—	—	198	—	131	—

pump (0.01 mL/min flow rate) through two hollow Teflon tubes having 2 mm internal diameter as shown in Figure 1. The left-hand lid is connected with a hollow metallic tube having a glass wool plug at the inner tip for putting the permeants, and the other end of which is connected with a anhydrous $CaCl_2$ tube to avoid forced permeation. Two hundred μL permeants were injected in each set of experiments and the diffusion study was conducted by monitoring the drift of difference frequency of the sensing and reference crystals with time.

RESULTS AND DISCUSSION

The diffusion of DMMP and water was studied using the modified diffusion cell as shown in Figure 1. As mass deposition occurs on the crystal, its characteristics change and results in shifting of frequency. The response of the detector was measured in terms of drift frequency (Hz) by us-

ing a differential piezoelectric oscillator circuit.[20,21] The circuit is very stable and can measure even a 2-Hz frequency change which corresponds to 1.7 ng of particulate mass deposition according to the Sauerbrey equation.[17,18] The shift of frequency is a function of time and increases as the diffusion process continues till saturation, which was monitored by an electronic stopwatch having a sensitivity of 10^{-2} s^{-1}. The modification of a previous cell[21] was required to perform the diffusion experiment at higher temperatures. Initially we thought that the reference and sensing crystal should be within the diffusion cell to nullify temperature interference, but the results were not promising or repeatable. It might be due to instantaneous sorption–desorption phenomena by the coating material itself, which affects the repeatability of the experiments. We planned a two-chamber diffusion cell in which one contained the membrane at high temperature and the other contained both the reference and sensing crystals at room temperature. Both the cham-
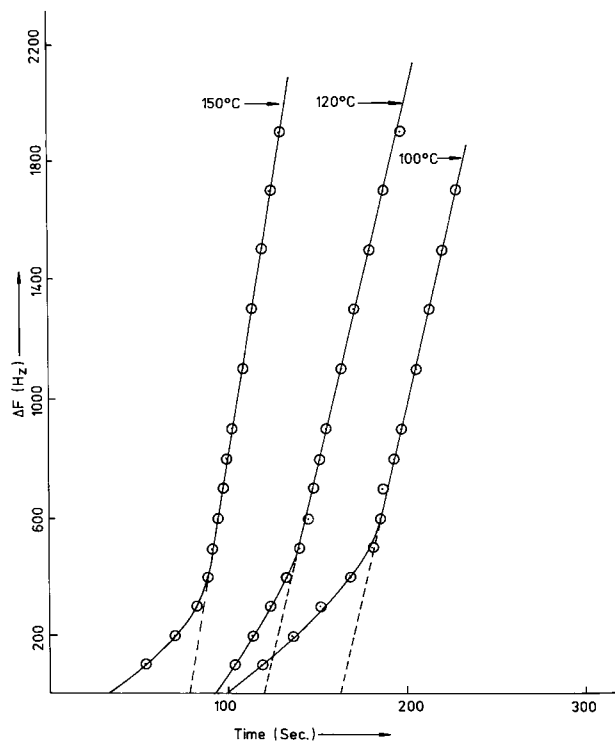
Figure 2 Typical sorption uptake response curve for DMMP.

bers were connected by a hollow Teflon tube. The study was conducted with PDMS membrane of thickness 0.037 cm at three different temperatures: 100, 120, and 150°C. The sorption uptake responses of the coated crystal in terms of drift frequency are given in Table I. In our previous article[21] we have already reported that the transport mechanism of water and DMMP is Fickian and independent of thickness of PDMS membrane, and the results have been supported by an independent technique (conventional sorption–desorption method).[10] There we observed that water diffuses at a slower rate than DMMP in a PDMS membrane at room temperature ($D_{water} = 8.6 \times 10^{-7}$, $D_{DMMP} = 1.0 \times 10^{-6}$). In the present experiment also, time-lag plots were obtained by plotting ΔF versus time (s). The representative plots for DMMP and water are shown in Figures 2 and 3, respectively. The intercept at the time axis by the linear portion of the curve is considered as permeation time (θ). The standard time-lag equation $D = L^2/6\theta$ (where L is the thickness of the membrane and D is the diffusion coefficient) is employed to calculate the diffusion coefficients. The results are presented in Table II. It is observed that water diffuses at a faster rate at high temperature than DMMP, which is contrary

to our previous investigation.[21] The falling diffusion coefficient with increasing water activity has been reported in terms of the statistical–mechanical clustering of the water molecules in PDMS membrane.[7,22] We feel this mechanism of clustering has been prevented with the PDMS membrane kept at high temperature, and thus diffusive species are expected to be only water monomers. Recently Watson and Baron[23] have ruled out the theory of water cluster formation in PDMS membrane, but we feel further study is required to come to a conclusion. As the temperature increases the diffusivity of the permeant molecules increases, because at high temperature the chain mobility of PDMS membrane increases, which results in higher fractional free volume (FFV) available for the permeant molecules. Thermal energy also contributes to the activation energy for the diffusion process. Temperature dependence diffusion coefficients have been used to calculate the activation energies for the diffusion processes by using the equation $D = D_0 e^{-Ed/RT}$. Slope of the Arhenious plot of ln D vs. $1/T$ (T in kelvin) (Fig. 4) provides the activation energies (Ed). Activation energies for DMMP and water in PDMS membrane are 19.58 and 20.92 KJ/mol, respectively. Watson and Baron[23] calculated that the energy to generate voids of sufficient size to accommodate the water molecules within PDMS is
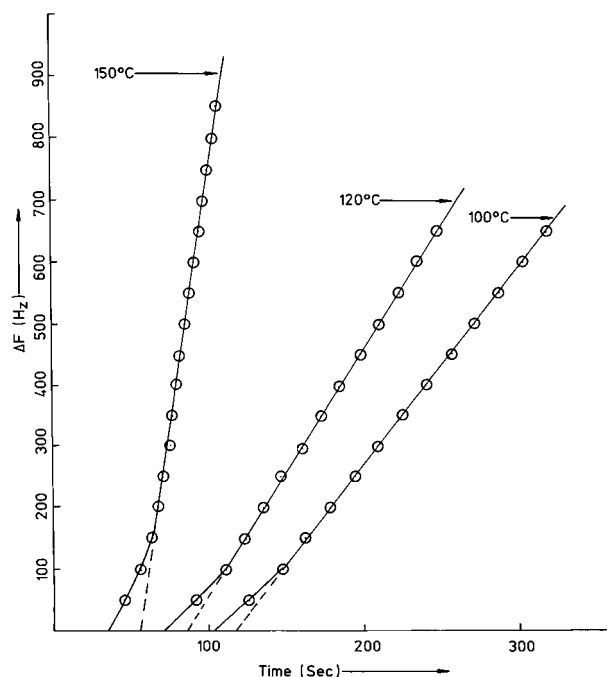

Figure 3 Typical sorption uptake response curve for water.

Table II   The Diffusion Coefficient and Permeability Values of DMMP and Water in PDMS Membrane

Temperature (°C)	θ (s)		$D \times 10^6$ (cm^2/s^{-1})		$P \times 10^8$ (cm^3 cm/ cm^2 s^{-1} atm)		α^* (P_{DMMP}/P_{water})
	DMMP	Water	DMMP	Water	DMMP	Water	
100	165.83	118	1.37	1.93	19.04	1.39	13.70
120	120.00	86	1.90	2.65	26.41	1.91	13.84
150	78.33	56	2.91	4.07	40.45	2.93	13.80

~ 14.5 KJ/mol, which is in close agreement with our experimental value.

The solubility coefficients of DMMP and water in PDMS membranes have been calculated by the gravimetric method.[24] The PDMS membranes were dried in a vacuum oven at 100°C for 1 h, dipped in DMMP and/or water, giving enough time to equilibrate (~ 80 h). Volume of sorption uptake responses by the PDMS membranes were used to calculate the solubility coefficient. It is observed that solubility coefficients of both DMMP and water do not increase significantly with increase of temperature, and the values are closer to the values obtained at room temperature.
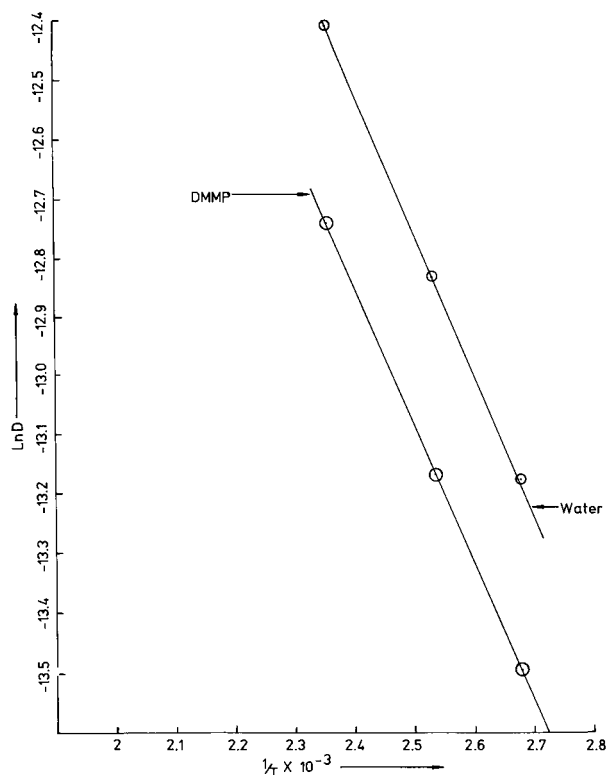
It may be attributed to the fact that the polymer–penetrant interaction is not affected significantly with temperature.[24] The values are 0.72×10^{-2} (400 mol/m^3, i.e., 7000 ppm by mass) and 13.9×10^{-2} (1176 mol/m^3, i.e., 17,880 ppm by mass) cm^3 cm^3 atm^{-1} for water and DMMP, respectively. A very high value of solubility coefficient for DMMP in PDMS indicates strong polymer–penetrant interaction and low value for water is mainly due to the hydrophobic behavior of the PDMS membrane. It is reported[25] that the sorption figure for filled PDMS membrane is ~ 200 mol/m^3. Hence our value is double, which halves the selectivity factor. This difference in sorption coefficient may be due to the presence of hydrophilic impurities.[23] The permeability coefficients calculated by using the equation $P = D \times S$ are reported in Table II. It is observed that the selectivity factor $P_{DMMP}/P_{water} > 13$. Although this selectivity value is quite high, for better results, especially for an analytical sample inlet system, nonfilled PDMS membrane[26] (sorption value for water is ~ 40 mol/m^3, ~ 700 ppm by mass) or extremely hydrophobic hexamethyl disiloxane[23] (water sorption is only 1 ppm) can be a better choice.

CONCLUSIONS

(1) A diffusion cell has been fabricated and employed for study of diffusion of chemical pollutants at high temperatures using a coated piezoelectric sensor; (2) temperature dependence diffusion coefficients for water and DMMP in PDMS membrane are also reported, which enables calculation of the activation energies; (3) permselectivity for DMMP over water is also reported ($\alpha^* = 13$); (4) this method is highly sensitive, economic, portable, and provides repeatable data and can be used to study the diffusion of other sorbates also if a proper (specific) coating material for the piezoelectric crystal can be found.

Figure 4   Arrhenius plots of ln D versus $1/T$ for water and DMMP.

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