

Sorption of Methane, Nitrogen, Carbon Dioxide, and Water in Matrimid 5218

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ABSTRACT: The sorption of the light gases CH₄, N₂, CO₂ as well as water into polymer films prepared from a commercial sample of 3,3'-4, 4'-benzophenone tetracarboxylic-dianhydride diaminophenylindane (Matrimid 5218) are measured. The light gas isotherms follow standard dual-sorption behavior for polymeric films with the Henry's Law coefficient correlated to the Lennard-Jones well depth pa-

rameter. Water sorption behavior was similar to rubbery polymers, that of significant adsorption into the polymeric matrix and was modeled by Henry's law exclusively. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2284–2289, 2010

Key words: Matrimid; sorption; carbon dioxide; nitrogen; methane; water; dual-sorption

INTRODUCTION

Polyimides are an important class of polymer for membrane gas separation, used, for example, in carbon dioxide and hydrogen sulfide separation during the sweetening of natural gas.¹ They exhibit a good combination of selectivity^{2,3} and permeability, and thus show potential for applications such as carbon dioxide capture.¹ The commercially produced 3,3'-4,4'-benzophenone tetracarboxylic-dianhydride diamino-phenylindane (BTDA-DAPI), commonly known as Matrimid 5218 (Fig. 1), is a polyimide widely used in industry because of its high glass transition temperature and good processibility.⁴ The ready availability of Matrimid as a commercial product means that it is often used in laboratory work as a polyimide indicative of those used for gas separation. However, there have been few quantitative studies on the sorption behavior of gases and condensable vapors within Matrimid films. Punsalan and Koros reported on CO₂ sorption in Matrimid as part of an aging study⁵ as well as a membrane thickness study,⁶ while Burns and Koros have examined Matrimid sorption for propane/propylene separation.⁷ Moore and Koros reported on CH₄ sorption as part of a mixed matrix

membrane study,⁸ and similarly Chung et al. has reported on CO₂ and CH₄ sorption in Matrimid as a result of a mixed matrix membrane with C₆₀.⁹ None of these studies explore water as a potential penetrant or consider the effects of temperature. Here, a quantitative study of gases CO₂, N₂, and CH₄ as well as water sorption in Matrimid 5218 over a range of temperatures is presented.

Matrimid, along with the majority of polyimides, is a glassy polymer at room temperature, because conditions are below the glass transition temperature of the polymer (T_g of Matrimid is 313 °C).⁵ As a consequence, Matrimid polymer films never reach thermodynamic equilibrium and the polymer chains are imperfectly packed. This generates excess free volume in the form of microscopic voids between polymer chains. Within these voids gases adsorb, increasing the solubility of gas within the polymer film. Therefore, the total concentration of absorbed gas within a glassy polymer film (C) can be described by¹⁰:

$$C = C_D + C_H \quad (1)$$

where C_H is sorption of gas within the microvoids, and can be approximated by the standard Langmuir adsorption relationship dependent on the gas pressure, p :

$$C_H = \frac{C'_H bp}{(1 + bp)} \quad (2)$$

C'_H is the maximum adsorption capacity, while b is the ratio of rate coefficients of adsorption and desorption, or Langmuir affinity constant, defined as:

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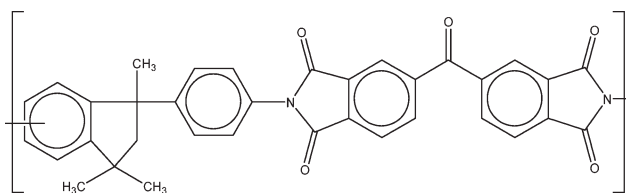


Figure 1 Chemical structure of BTDA-DAPI 3,3'-4,4'-benzophenone tetracarboxylic-dianhydride diaminophenylin-dane (Matrimid 5218).

$$b = \frac{C_H}{(C'_H - C_H)p} \quad (3)$$

C_D is the concentration of gas dissociated within the polymer matrix and is proportional to the gas pressure through the Henry's Law constant (K_D). Hence, the dual-mode sorption of gases with glassy polymer films is written as:

$$C = K_D p + \frac{C'_H b p}{(1 + b p)} \quad (4)$$

As CO₂ is a non-ideal gas at relatively low pressure and temperatures, there are also circumstances where it is useful to present this relationship in terms of the gas fugacity, f :

$$C = K_D f + \frac{C'_H b f}{(1 + b f)} \quad (5)$$

The Henry's Law coefficient within this expression can be correlated with the Lennard-Jones potential well depth parameter (ϵ/κ) for the penetrating gas^{11,12}:

$$K_D = K_{DO} e^{\frac{m\epsilon}{\kappa T}} \quad (6)$$

The parameter, m , is a constant independent of the penetrant or the nature of the penetrating medium. Toi et al.¹² present data that shows that $m = 6.67 \pm 0.5$. The parameter K_{DO} is a function of the medium through which the species penetrates, but Toi et al.¹² show that the range of values for this parameter is also quite limited, ranging from 0.0072 cm³ (STP)/cm³.atm for amorphous polyethylene to 0.0298 cm³ (STP)/cm³.atm for liquid benzene.

In the case of strongly condensing vapors, such as water, the Langmuir model may not be appropriate given the possibility of multilayer adsorption within the microvoids. Park¹³ puts forward a simplified model for the concentration of water within the glassy membrane when multilayer adsorption occurs:

$$C = K_D p + \frac{C'_H b p}{1 + b p} + K_C K_D^n \frac{p^n}{n p_0} \quad (7)$$

where n is the number of water molecules within the microvoid, K_C the equilibrium constant for the adsorption reaction of a free water molecule to the water layer and p_0 the saturation pressure. Alternatively, a Brunauer-Emmett-Teller (BET) model may be a more appropriate isotherm to apply in such situations.¹⁴

This study consists of solubility measurements of N₂, CH₄, and CO₂ within Matrimid 5218 at four temperatures, 20, 35, 55, and 75°C, along with the solubility of water within Matrimid, at temperatures 35 and 55°C. The resulting isotherms are analyzed by modified dual-sorption models, with the respective parameters determined.

EXPERIMENTAL

Matrimid 5218 (Huntsman Chemical Co.) was cast as flat dense sheets from a filtered 2.5 w/v% dichloromethane (Ajax Finechem, AR grade) solution in casting rings on glass plates. The polymeric films were first dried at ambient temperature for 24 h and then further dried at 100°C for 24 h under vacuum to ensure complete solvent evaporation. The films were then annealed at 150°C for another 48 h under vacuum. On completion of the annealing process, the films were cooled slowly to room temperature under vacuum conditions, ~6 h, and during storage were kept in a moisture free environment. This produced consistent films of thicknesses ~ 40 μm,

Sorption measurements were conducted on a Gravimetric Sorption Analyzer (GHP-FS, with a Cahn D-200 balance, VTI Scientific Instruments, Florida). For sorption isotherms of N₂, CH₄, and CO₂ over the range of temperatures, the instrument was operated in static mode. Initially, Matrimid was placed in the sample chamber and the system was evacuated and heated to 120°C for 120 min to remove all air and water vapor from the polymeric matrix. The sample chamber was then set to the desired temperature and penetrant gas was introduced into the chamber at incremental pressures. At each pressure level, the system was allowed to equilibrate until a constant mass was recorded, taking up to 120 min each time. By increasing the pressure of the gas in the sample chamber in an incremental manner, penetrant isotherms as a function of penetrant pressure were determined. Desorption of the penetrant gas was then measured by similarly reducing the penetrant gas pressure in increments and again allowing the total mass of the system to reach equilibrium at each point. After measuring both sorption and desorption isotherms, the sample chamber was again evacuated. The same procedure as above was then undertaken with helium gas,

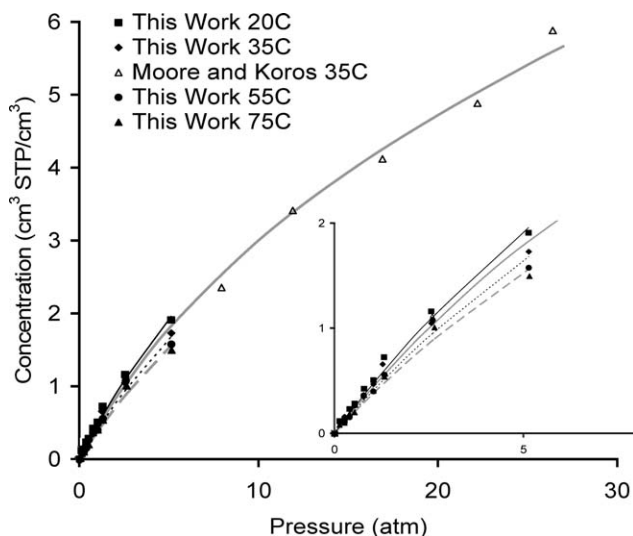


Figure 2 N_2 sorption isotherm within Matrimid at various temperatures. Data points represented experimental data from this work (closed symbols) and from Moore and Koros⁸ (open symbols). Lines are simulations of eqs. (5) and (6) using data from Table I. The inset graph shows the data at low pressures in more detail.

which can be assumed to have no adsorption to Matrimid. This allows the buoyancy correction to be verified.

For water isotherms, the Gravimetric Sorption Analyzer was operating in a flow mode, which provides a more accurate measurement of condensable vapors.¹⁵ The standard degassing procedure as above was undertaken to remove air and water vapor. Helium, the carrier gas, was then allowed to flow through the Matrimid sample chamber at slightly greater than atmospheric pressure. The helium entered from two streams, one dry, the other passed through a water bubbler set at the temperature of the experiment, which saturated the helium with water. Relative humidity within the sample chamber was achieved by varying the flowrate ratio of the dry and wet gas streams, and by incrementally adjusting this ratio, different relative humidities were obtained. The total sample mass was allowed to equilibrate, taking approximately 1 h, before the flow rate was adjusted to the new relative humidity setting. Both adsorption and desorption isotherms of the different vapors within Matrimid were measured, and the balance was kept free of condensation via nitrogen purge gas.

RESULTS AND DISCUSSION

The N_2 , CH_4 , and CO_2 isotherms of Matrimid 5218 for the four temperature ranges are shown in Figures 2, 3, and 4, respectively. Also comparable data available from both Moore and Koros⁸ and Chung et al.⁹ are shown. The data is clearly consistent for

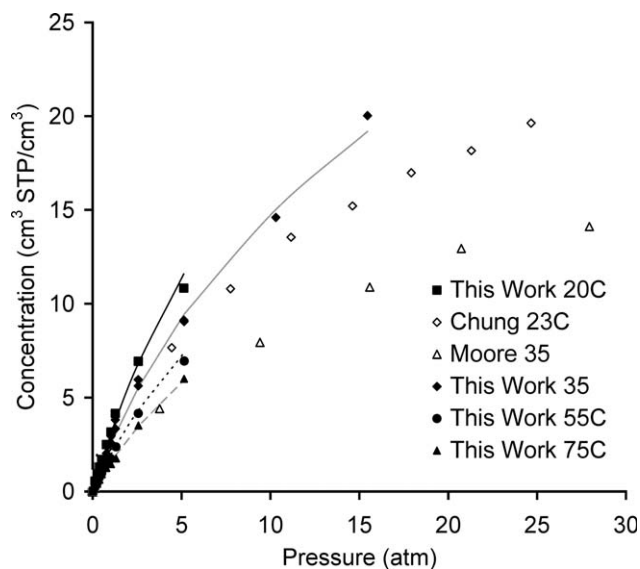


Figure 3 CH_4 sorption isotherm within Matrimid at various temperatures. Data points represented experimental data from this work (closed symbols) and from Moore and Koros⁸ (open symbols). Lines are simulations of eqs. (5) and (6) using data from Table I.

N_2 and CO_2 but shows some variation for methane. This might reflect differences in the membrane casting methods or the effects of physical aging or alternatively differences in penetrant gas purity or the elapsed time at each pressure level during sorption measurement.

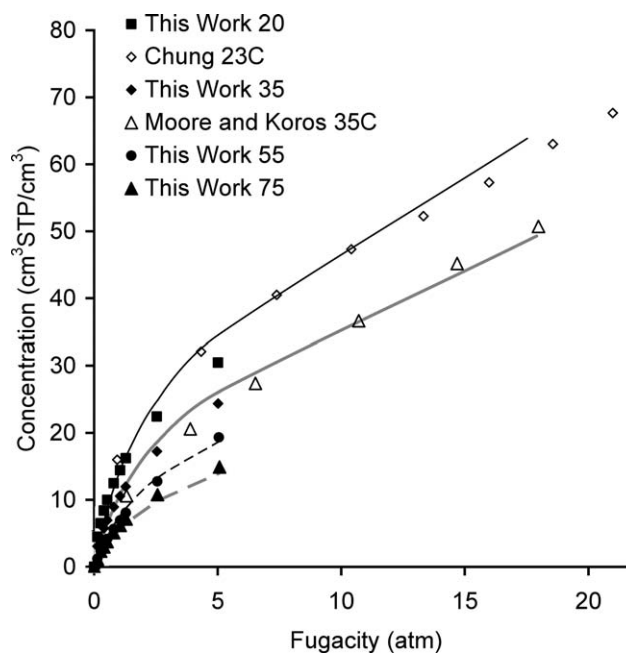


Figure 4 CO_2 sorption isotherms within Matrimid at various temperatures. Data points represented experimental data from this work (closed symbols) and from Moore and Koros⁸ and Chung et al.⁹ (open symbols). Lines are simulations of eqs. (5) and (6) using data from Table I.

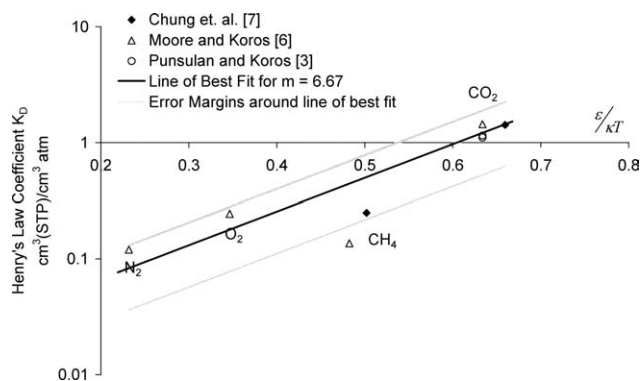


Figure 5 The Henry's Law coefficient, K_D as a function of the Lennard-Jones Well potential ($\epsilon/\kappa T$). Data is taken from Moore and Koros⁸ and Punsalan and Koros² at 35°C and Chung et al.⁹ at 23°C. Error margins are for ± 0.01 cm³ (STP)/cm³.atm around the value of $K_{DO} = 0.018$ cm³ (STP)/cm³.atm.

The chemical associations between CO₂ and Matrimid are more thermodynamically favorable and hence the sorbed CO₂ concentration is substantially higher than that for N₂ and CH₄ at similar pressures. CO₂, N₂ and CH₄ isotherms all demonstrate standard dual-sorption behavior—that of a rapid increase in gas concentration at low pressures, which tapers off at higher pressures to an almost linear relationship.¹⁰ At low pressures, the microvoid space within the polymeric matrix is rapidly filled. As the pressure of the gas increases, free microvoid space becomes limited and the concentration increase is reduced to the sorption of gas in the polymeric matrix only. This follows Henry's Law, hence the almost linear relationship at high pressures. The desorption isotherms for each of the gases provide the same behavior.

Least squares optimization of this dataset to fit eq. (4) initially resulted in large error margins around the adjustable parameters, indicating that there were too many degrees of freedom. To reduce this error, the Henry's Law parameter, K_D was determined from eq. (6). The parameter $m = 6.67 \pm 0.5$ was used and Lennard-Jones parameters obtained from Poling et al.¹⁶ To determine an appropriate value of K_{DO} , Henry's Law parameters available in the literature^{2,8,9} for penetration of O₂, N₂, CH₄ and CO₂ into

Matrimid were analyzed. Least squares analysis of the six data points available indicated a value of 0.018 ± 0.01 cm³ (STP)/cm³.atm (see Fig. 5). This value is well within the range predicted by Toi et al.¹² It is notable that the data for methane is somewhat lower than that available for other gases.

To reduce the number of adjustable parameters further, the maximum Langmuir capacity C'_H was assumed to follow an Arrhenius relationship with temperature:

$$C'_H = C'_{Ho} e^{\frac{-\Delta H_s}{RT}} \quad (8)$$

The regression analysis showed that temperature variation in the Langmuir affinity constant, b , was minimal.

Finally, to maximize precision, the data available from Chung et al.⁹ and Moore and Koros⁸ for CO₂ and N₂ were included in the regression analysis. This was not possible for methane, as there was insufficient consistency between the results from the three research groups.

Results from a least squares analysis with these datasets and these constraints are shown in Table I for CO₂, CH₄ and N₂. Results for both pressure [eq. (4)] and fugacity [eq. (5)] based values for CO₂ are shown. The resulting concentration predictions have been added to Figures 2 to 4.

Toi et al.¹² provide a correlation between the maximum Langmuir capacity C'_H for CO₂ at 35°C and the glass transition temperature. This correlation would suggest a value for Matrimid ($T_g = 313^\circ\text{C}$) of approximately 40 cm³ (STP)/cm³.atm at 35°C. Our predicted value of 27.5 cm³ (STP)/cm³.atm is a little lower. Punsalan and Koros⁵ obtain values of 28.9 and 32.9 for aged and unaged Matrimid films respectively, which is more consistent. The Langmuir affinity coefficient can be correlated with the critical temperature of the penetrant.¹⁷ This suggests that b should increase in the sequence N₂/CH₄/CO₂ as observed. Indeed, our predicted values are all within the error bounds of this correlation. The value for CO₂ of 0.395 is consistent with the values quoted by Punsalan and Koros⁵ of 0.38 for an unaged film and 0.40 for an aged film.

All heats of sorption are exothermic. The heat of sorption strongly favors CO₂, then CH₄ and finally N₂. Hence, in a gas mixture CO₂ adsorption to

TABLE I
Dual-Sorption Parameters, C'_{Ho} (cm³(STP)/cm³), b (atm⁻¹) and Heat of Adsorption (kJ mol⁻¹) Pressure Based for CH₄, N₂, and CO₂ (Including Fugacity Based) in Matrimid 5218

	CH ₄	N ₂	CO ₂ (pressure basis)	CO ₂ (fugacity basis)
C'_{Ho}	0.264 ± 0.081	1.40 ± 0.58	0.080 ± 0.031	0.078 ± 0.035
ΔH_s	-11.0 ± 0.8	-3.4 ± 1.0	-14.9 ± 0.97	-15.3 ± 1.1
b (atm ⁻¹)	0.114 ± 0.007	0.0720 ± 0.0052	0.496 ± 0.033	0.395 ± 0.030

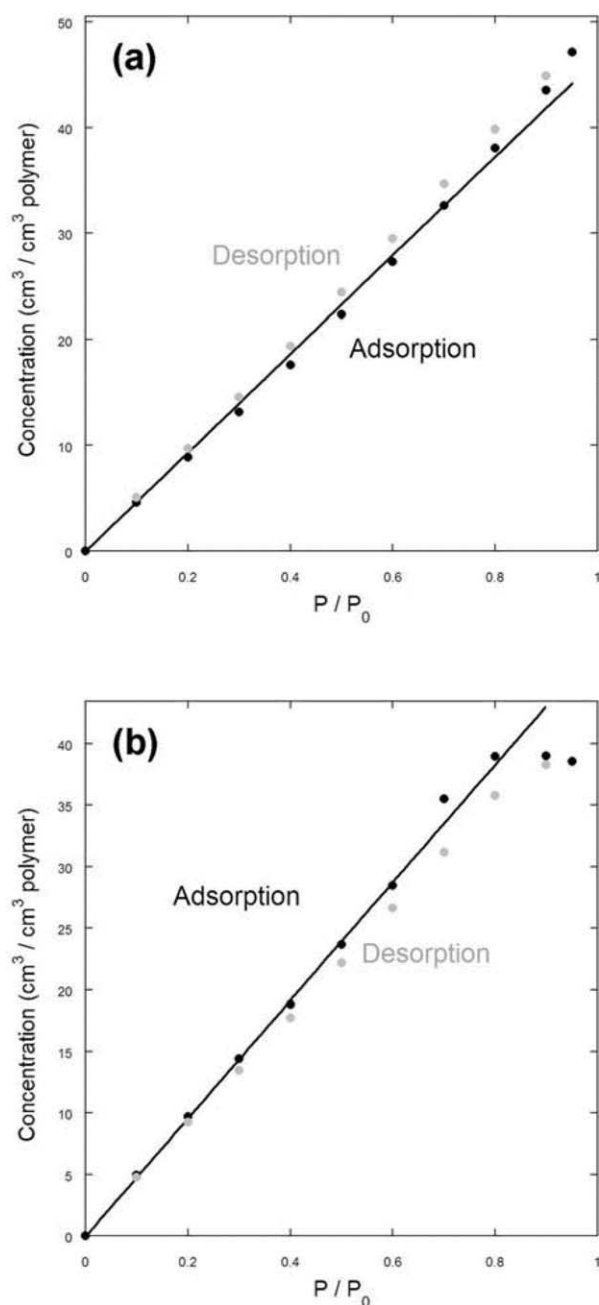


Figure 6 Matrimid sorption isotherms for H₂O, at 35°C (a) and 55°C (b). Lines are simulations of eq. (6) using a Lennard-Jones parameter of 493.

Matrimid microvoids is more probable than either N₂ or CH₄.

The sorption of water into Matrimid at 35 and 55°C is shown in Figure 6 and does not display standard gas dual mode-sorption behavior for glassy polymers. Rather, the isotherm is typical of penetrant sorption into rubbery polymers, which occurs exclusively in the polymeric matrix.¹⁸ This would suggest that water strongly sorbs within this region for Matrimid, and only at very high partial pressures does adsorption to the microvoids contribute to the

measured isotherm. The lack of significant water sorption to the microvoid volume may reflect the hydrophobicity of Matrimid, restricting adsorption. Hence, adsorption in the microvoids (Langmuir) is considered negligible and the isotherms are fitted exclusively to Henry's Law. The behavior observed at very high relative partial pressure is excluded from the fit because there is not enough data points to allow accurate modeling of microvoid adsorption models. The Henry's Law constants determined from the lower pressure data are 957 and 342 cm³(STP)/cm³ atm at 35°C and 55°C, respectively.

These Henry's Law constants are high, relative to the other gases reported. This is a product of the small water molecule easily residing between polymer chains within the polymeric matrix. Estimating the Henry's Law constant for water from eq. (6), based on the Lennard Jones potential parameter of 809.1 reported by Poling et al.,¹⁶ reveals a value of 720,000 at 35°C, which is three orders of magnitude greater than the experimental value. However, it has been recognized that there can be inconsistencies in reported Lennard Jones potential parameters based on determination methodology,¹⁹ as well as shortcomings in the theory given that there is no accounting for molecular shape.²⁰ Tee et al.²¹ develops a number of correlations to overcome this inconsistency, and a Lennard Jones potential parameter of 460 for water was estimated based on this approach. Back calculation of the Lennard Jones potential parameter from the experimental Henry's Law constant, assuming $m = 6.67$ and $K_{DO} = 0.018$ indicates a value of 495 ± 9 which is more consistent with the value generated from the Tee correlation.

The desorption isotherm of water for both temperature systems is almost identical to the adsorption isotherm, implying that as the relative humidity of the surrounding gas is reduced, water evaporation from the polymer is unrestricted.

CONCLUSION

To conclude, the sorption of CH₄, N₂, CO₂, and water in Matrimid 5218 was measured. The gases CH₄, N₂, and CO₂ followed standard dual-sorption behavior with Langmuir adsorption, which favored CO₂ adsorption compared to CH₄ and N₂. Water is strongly absorbed into the polymer matrix, with the determined Henry's Law constant suggesting a lower Lennard Jones potential parameter for water than that commonly quoted.

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