Sorption of CO_2/CH_4 Mixtures in Poly(phenylene Oxide) and a Carboxylated Derivative

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SYNOPSIS

The sorption of CO_2 and CH_4 and their binary mixtures in poly(phenylene oxide) (PPO) and its carboxylated derivative (CPPO) is reported. All mixed gas data are accurately described by the dual mode sorption model, which predicts mixed gas sorption on the basis of pure gas sorption parameters. The present paper extends the mixed gas sorption data base to include polymers having a wide range of permeabilities and chemical structures. The confirmed accuracy of the model for these systems provides strong support for applying the mixed gas dual mode sorption model to any gas/polymer system. A numerical simulation of the mixed gas sorption experiment is also presented which greatly simplifies the experimental procedures used to maintain the partial pressure of one of the gas components at a constant value over the course of a sorption isotherm measurement. By establishing the appropriate amounts of each gas component which are added to the polymer sample chamber of the sorption cell, the mixed gas apparatus simulator (MIGAS) can be used to maintain the partial pressure of one of the components to within 1% of the desired value.

INTRODUCTION

Current models for the solubility, diffusivity, and permeability of pure gases in glassy polymers generally provide qualitatively accurate predictions of membrane performance, but often fall short when applied to the actual mixed gas operating conditions of gas separators.[1,2] The modeling of mixed gas transport is seriously complicated by the limited availability of mixed gas sorption data. Without these data, the accuracy of models for predicting mixed gas solubility cannot be verified. Consequently, any deviations between mixed gas permeability data and mixed gas permeability model predictions cannot be addressed in terms of the separate solubility and diffusivity factors which govern the permselective properties of polymers. The present paper extends the mixed gas sorption data base for the CO_2/CH_4 system and demonstrates the effective use of the dual mode sorption model for describing the sorption of gas mixtures in glassy polymers. These results are applied to a study of mixed gas permeability and its deviations from various mixed gas permeability models in a recent paper.[1]

BACKGROUND AND THEORY

The permeation of a gas through a polymer membrane is a coupled process involving the dissolution and diffusion of the gas in the polymer matrix. It is convenient to represent the permeability as the product of an *average* diffusivity D and solubility S:

$$P = DS \qquad (1)$$

The kinetic factor (D) and thermodynamic factor (S) can be separated by measuring directly the permeability and solubility of a gas/polymer system and then calculating the diffusivity. Equation (1) is easily extended to gas mixtures to describe membrane selectivity:

$$\alpha^*_{AB} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B}\right]\left[\frac{S_A}{S_B}\right] \qquad (2)$$

where α_{AB}^* is the *ideal separation factor* for gases A and B. The factors comprising α_{AB}^* are the diffusivity selectivity and solubility selectivity, respectively. By this partitioning of permeability and selectivity into its thermodynamic and kinetic components, the dominant permeability and selectivity factors can be determined for a given gas/polymer system.

Solubility and Solubility Selectivity

The dual mode theory of gas sorption has been used extensively to describe the solubility of gases in glassy polymers.[3-7] The fundamental assumption of the dual mode sorption theory is the existence of two subtly distinct populations of gas molecules in a polymer matrix. One of these gas populations is dissolved by the polymer molecules essentially as it would be in a liquid or a rubber. The remaining gas molecules are presented in the nonequilibrium molecular scale gaps which are characteristic of glassy polymers. The term *sorption* is used to describe the uptake of gases into *both* of these glassy polymer environments. The model denotes these modes of gas sorption as

$$C_A = C_{D_A} + C_{H_A} \qquad (3)$$

where C_A is the total concentration of a sorbed gas A in the polymer. It is comprised of C_{D_A} and C_{H_A}, representing the concentrations of gas molecules in the so-called Henry's Law, or dissolved, and the Langmuir, or hole-filling environments, respectively. In terms of gas pressure, the model is written as

$$C_A = k_{D_A} p_A + \frac{C'_{H_A} b_A p_A}{1 + b_A p_A} \qquad (4)$$

where k_{D_A}, C'_{H_A}, and b_A are the pure component values of the Henry's law, Langmuir capacity, and Langmuir affinity parameters, respectively, as determined by pure gas sorption measurements. More detailed analyses of the dual mode sorption parameters are given elsewhere.[2-9]

The dual mode model is easily extended to include gas mixtures.[10] In terms of partial pressures of gases A and B, the expressions for mixed gas sorption are usually written as

$$C_A = k_{D_A} p_A + \frac{C'_{H_A} b_A p_A}{1 + b_A p_A + b_B p_B} \qquad (5a)$$

$$C_B = k_{D_B} p_B + \frac{C'_{H_B} b_B p_B}{1 + b_A p_A + b_B p_B} \qquad (5b)$$

The model predicts a reduction in the sorption of any gas, at a fixed partial pressure, as the partial pressure of a second gas is increased. Sanders and Koros[11,12] reported that sorption isotherms of binary mixtures of CO_2/N_2O and CO_2/CH_4 in poly(methyl methacrylate) (PMMA) are predicted to within 2% by this model. However, prior to the present research, $PMMA/CO_2/N_2O$ and $PMMA/CO_2/CH_4$ were the only systems in which mixed gas sorption had been measured. Because PMMA is not generally regarded as a viable polymer for membrane applications due to its low permeability, further verification of the mixed gas dual mode sorption model in high flux materials such as PPO is essential to a thorough investigation of mixed gas transport in potentially useful membrane materials.

As with pure gas permeability, the permeability of a component in a gas mixture is the product of its solubility and diffusivity in the mixture. The importance of mixed gas sorption measurements lies in the fact that, *for any polymer/gas A/gas B system, confirmation of mixed gas dual mode sorption behavior implies that any differences between mixed gas permeability model predictions and mixed gas permeability data are directly attributable to deficiencies in the modeling of mixed gas diffusivity.* The resolution of any such mixed gas diffusivity modeling problems is important to a complete understanding of the permeation process.

The scarcity of mixed gas sorption data is due primarily to the difficulty of the measurement. Since the pressure of both gases has an effect on the sorption of each component, the representation of mixed gas sorption data requires 3-dimensional plots unless the partial pressure of one component can be held constant. This is difficult because of the effect of competitive sorption on the experimental partial pressures. For example, consider a polymer at equilibrium with 4.9 atm of gas A. Upon introduction of 2 atm of gas B to the system, some of the added gas B will be sorbed into the polymer, while some of the sorbed gas A will be displaced from the polymer and into the gas phase. The partial pressure of gas A will therefore increase to, say, 5.0 atm. Further addition of gas B will continue to increase the partial pressure of gas A unless some of the gas mixture is removed. Sanders[9,11] devised a method whereby the amount of gas removed from the polymer-containing chamber for gas chromatographic (GC) analysis, after the first addition of pure gas B to the system, is enough to return the partial pressure of gas A to 4.9 atmospheres. If the next amount of gas B added to the polymer chamber is carefully chosen, the partial pressure of gas A will again increase to 5.0 atm.
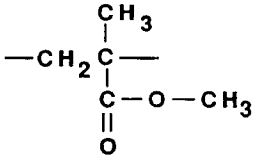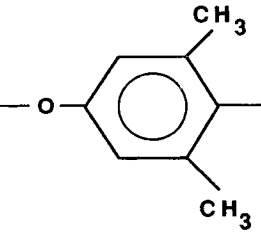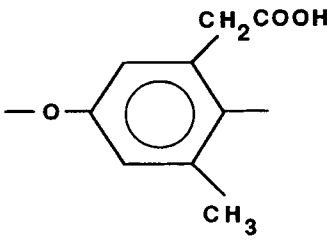
By balancing the withdrawal of GC samples with the addition of gas B, the partial pressure of gas A can be maintained at or near 5.0 atm during the entire experiment.

The technique described above is very tedious, and requires a fair amount of guesswork and experience. If the desired constant partial pressure is allowed to vary significantly, the sorption data can become quite scattered. This is especially serious when measuring very low sorption levels, which are frequently encountered as more and more of a low sorbing component is displaced from the polymer by a high sorbing gas. Because of these experimental difficulties, it is essential that the polymers chosen for mixed gas sorption measurements represent a wide range of materials, both in terms of chemical character and membrane performance. If the mixed

gas extension of the dual mode model can be verified for these representative materials, the adequacy of the mixed gas dual mode sorption model in untested polymers then becomes a reasonable assumption.

The polymers chosen for this study of mixed gas sorption were poly(phenylene oxide) (PPO) and a carboxylated PPO (CPPO). PPO has previously been proven as a high flux, low selectivity material, while CPPO possesses moderate permeability and selectivity.[13,14] Table I shows that, along with previous data for PMMA, the PPO/CO_2/CH_4 and CPPO/CO_2/CH_4 data should bracket a wide range of permselective properties of glassy polymers. These three polymers also encompass a wide range of polarities, with PMMA containing a high concentration of polarizable carbonyl substituent groups and PPO containing no such polar character.[15] The de-

Table I Permselective Properties[a] of the Polymers Currently in the Mixed Gas Sorption Data Base

Polymer	p_{CO_2}[b]	$\alpha_{CO_2CH_4}$	Carbonyl Concentration (g/cc)
 CH_3 | —$CH_2$$C$— | C—O—CH_3 || O PMMA	0.357	62	0.325
PPO	45	15	0.0
CPPO	23	20	0.12

[a] Barrer = 10^{-10} [cc(STP)cc/cm^2 s cm Hg].
[b] Total pressure 20 atm, equimolar CO_2/CH_4 mixture, 35°C.

sired range of both permselective properties and chemical character for the mixed gas sorption data base is thus achieved.

EXPERIMENTAL

Carboxylated PPO (CPPO)

Carboxylated PPO was prepared according to the organometallic scheme of Chalk and Hay.[16] In this method, PPO is first reacted with butyl lithium to form an intermediate material which is substituted primarily at the methyl side chain position. The lithiated polymer is further reacted with CO_2 and then acidified to form the carboxylated derivative:
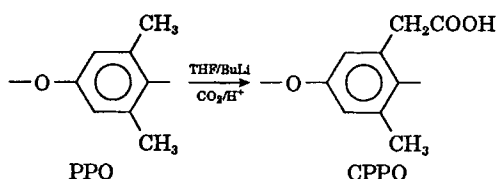
The degree of carboxylation can be controlled by varying the butyl lithium/PPO ratio and the reaction time. The modified PPO used in the mixed gas sorption measurements contained an average of 0.22 carboxyl groups per repeat unit, as determined by titration with ethanolic KOH in pyridine.

Casting of Polymer Films

Dense films of PPO were cast from 5% solutions in chloroform, while CPPO films were cast from THF solutions. All casting solutions were filtered and centrifuged at 12,000 rpm for 2 h to remove any crosslinked material or undissolved impurities. Films were cast by pipetting 2–5 cc of casting solution onto a leveled glass plate which was heated to just below the boiling point of the solvent. A circular steel ring was used as a mold for the films. The casting ring was then covered with filter paper to keep out dust and to prevent the "orange peel" effect caused by rapid solvent evaporation. After 20 min, the films were solid and relatively free of solvent. They were released from the glass plate by immersion in distilled water, and dried under vacuum for 24 h at 150°C.

Pure Gas Sorption

The techniques for the measurement of pure gas sorption are well documented in the literature[9,17] and will not be explained in detail here. Pure gas sorption measurements for PPO and CPPO were made using chambers A and B of the mixed gas sorption cell, as discussed below.

Mixed Gas Sorption

The mixed gas sorption apparatus used in this study is shown in Figure 1. A schematic of the entire mixed gas sorption system is given in Figure 2.[9] Design considerations and details of the apparatus are addressed by Sanders, who developed the mixed gas sorption techniques.[9,11] The construction of the
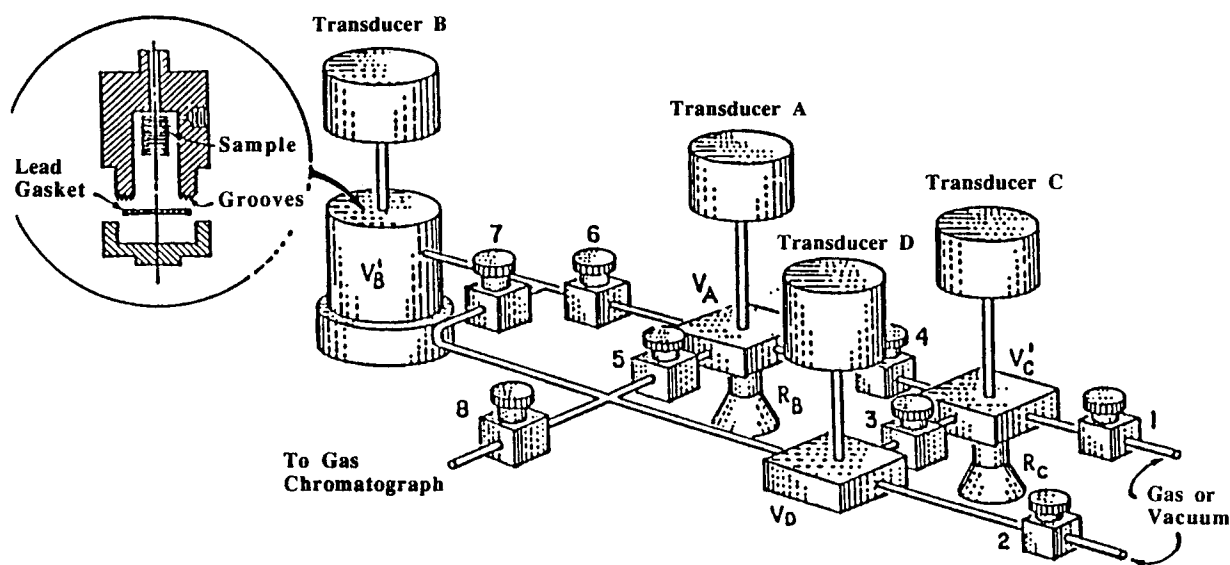

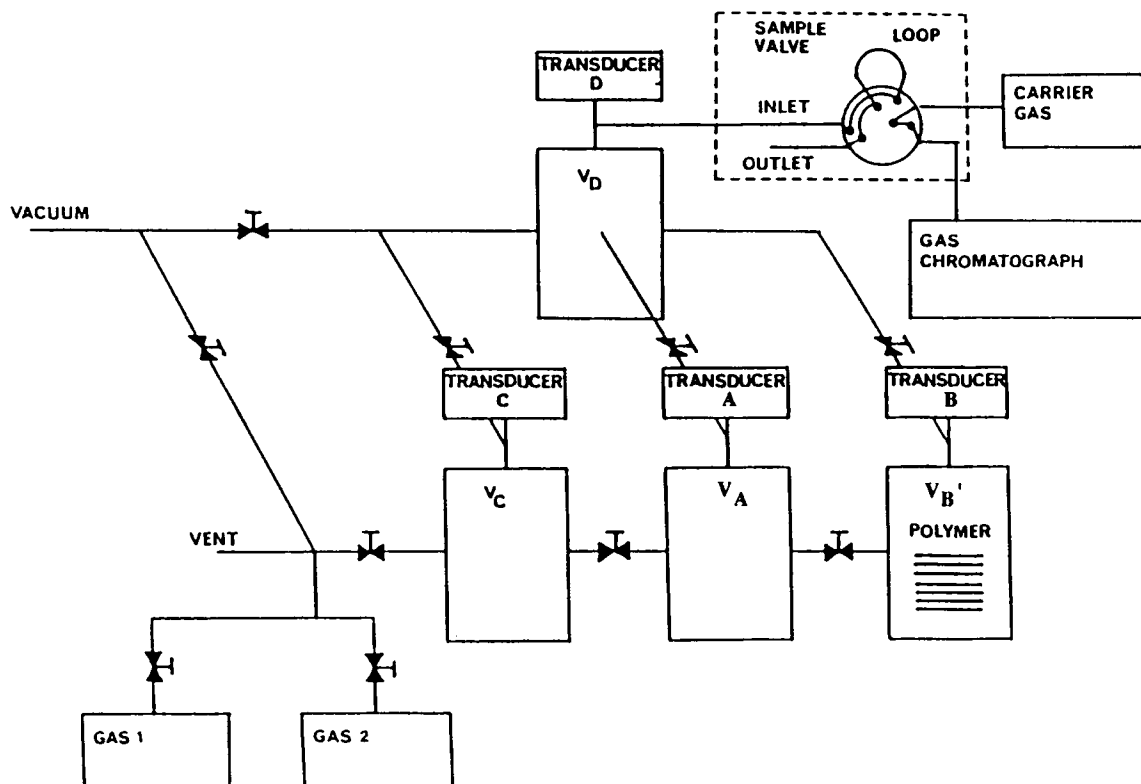**Figure 1** Mixed gas sorption cell.

Figure 2   Overall schematic of the mixed gas sorption system.[9]

mixed gas cell is similar to that of a standard dual transducer, pressure decay, pure gas sorption cell, except for the additional chambers which are used for preparation and GC sampling of gas mixtures. Gas analyses were performed using a Tracor Model 570 gas chromatograph fitted with a thermal conductivity detector (TCD).

The mixed gas cell can be used for both pure and mixed gas sorption measurements. Pure gas measurements are made simply by using V_A as the reservoir volume and V_B as the polymer sample chamber. Mixed gas sorption measurements can be made using two different methods, which differ in the manner in which the mixed gas environment is introduced to the polymer chamber. The first method involves the preparation of gas mixtures, using chambers A and C, and injecting this mixture into the evacuated sample chamber. The second method involves the injection of only pure gases into the sample chamber. Both methods of injection, including the mass balance sorption calculations, are discussed in detail by Sanders.[9,11,12]

The pure component injection method was employed in this study, since it allows maintenance of partial pressure of one component at a constant value, thereby eliminating the need for three-di-

mensional data plots (i.e., gas concentration vs. p_A and p_B). This approach facilitates comparison of mixed gas data with the mixed gas dual mode sorption model.[9,11] As discussed previously, the introduction of a second gas B to a glassy polymer in equilibrium with gas A causes some the sorbed gas A to be "kicked out" of the polymer by competitive sorption with gas B. The partial pressure of gas A increases as more and more gas B is added to the system. By withdrawing a carefully chosen amount of the gas mixture after sorption equilibrium is reached, the partial pressure of gas A can be restored to its original value. This small sample is then used for GC analysis of the gas mixture composition. The amount of sample which must be withdrawn following each addition of gas B has previously been determined by a trial and error procedure, aided by familiarity with the gas/polymer system being studied and the mixed gas apparatus itself. A computer simulation of the mixed gas sorption technique, MIGAS, will be discussed later which eliminated much of the guesswork associated with the constant partial pressure technique.

A typical mixed gas sorption experiment, for a constant gas A partial pressure of 5 atm, is conducted as follows:

(1) Using V_A and V_B, measure the sorption of pure gas A up to, say, 4.9 atm. Evacuate V_A, and pressurize with pure gas B to at least 10 atm higher than the pressure in the sample chamber V_B. Using the MIGAS program, determine the required amount of gas B added to V_B to increase the partial pressure of gas A to 5.0 atm. Open valve 6 and slowly bleed in this amount of gas B by monitoring the initial and final pressures of gas B in V_A.

(2) Evacuate V_A and V_D, the transfer lines to the GC, and the sample loop for at least 1 h prior to sampling of the gas mixture. (A liquid nitrogen-cooled vacuum trap should be used to prevent vacuum pump oil vapors from contaminating the transfer lines. Condensation of oil vapors on the transfer line walls can cause absorption of CO_2 from the CO_2/CH_4 mixture sample, leading to inaccurate gas composition analyses). After the pressure in V_B has come to equilibrium, close valves 2 and 4, and withdraw gas from the sample chamber into V_A and V_D until the pressure in V_D reaches about 1.0 psia. The gas sample is then analyzed using the gas chromatograph.

(3) Calculate the equilibrium partial pressure of each gas, and determine the sorption of each component by constructing a mass balance for both gases. If p_A is not within 5% of the desired partial pressure, it may be necessary to add more of gas B (if p_A is too low) or withdraw more of the gas mixture (if p_A is too high). However, using the MIGAS program practically eliminates this "backtracking" step.

(4) Using MIGAS to account for the amount of withdrawn GC sample, calculate the next in-
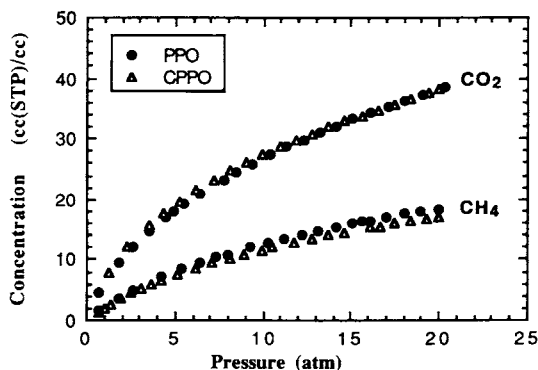
Figure 3 Pure gas sorption isotherms for PPO and CPPO.

Table II Dual Mode Sorption Parameters for CO_2 and CH_4 in PPO and CPPO

Polymer	k_D (cc(STP)/cc atm)	C'_H (cc(STP)/cc)	b (atm^{-1})
(A) CO_2			
PPO	0.8490	25.86	0.2395
CPPO	0.7918	26.28	0.2852
(B) CH_4			
PPO	0.2674	19.10	0.1077
CPPO	0.2981	15.53	0.1254

crement of gas B required to restore the partial pressure of gas A to 5.0 atm.

(5) Close valve 5, evacuate V_A through valve 1, and repressurize V_A with gas B to a pressure at least 10 atms higher than that of the total pressure in V_B. Continue adding gas B in increments determined by MIGAS until p_B reaches the desired level. The mixed gas sorption cell is limited to a total pressure of about 20 atm, since the reservoir transducers have a pressure limit of about 35 atm.

RESULTS AND DISCUSSION

Pure Gas Sorption

For the purposes of consistent comparison of transport properties, the sorption in all modified PPO's was measured using samples which had been conditioned under 20 atm of CO_2 for 24 h, as done in previous studies.[6,8-12] The choice of 20 atm for the conditioning pressure was influenced by the pressure range restrictions of mixed gas sorption measurements. The mixed gas sorption apparatus used in this study is designed for accurate sorption measurements up to only approximately 20 atm total pressure. The pure CO_2 and CH_4 sorption isotherms for PPO and CPPO are shown in Figure 3. Dual mode sorption parameters are presented in Table II.

Mixed Gas Sorption

The sorption of CO_2/CH_4 mixtures was measured in PPO and in CPPO. Figure 4(a) shows the PPO sorption isotherms for both components, in which the partial pressure of the other component was maintained at approximately 5 atm, compared with the pure gas sorption isotherms. Figures 4(b)-(c)
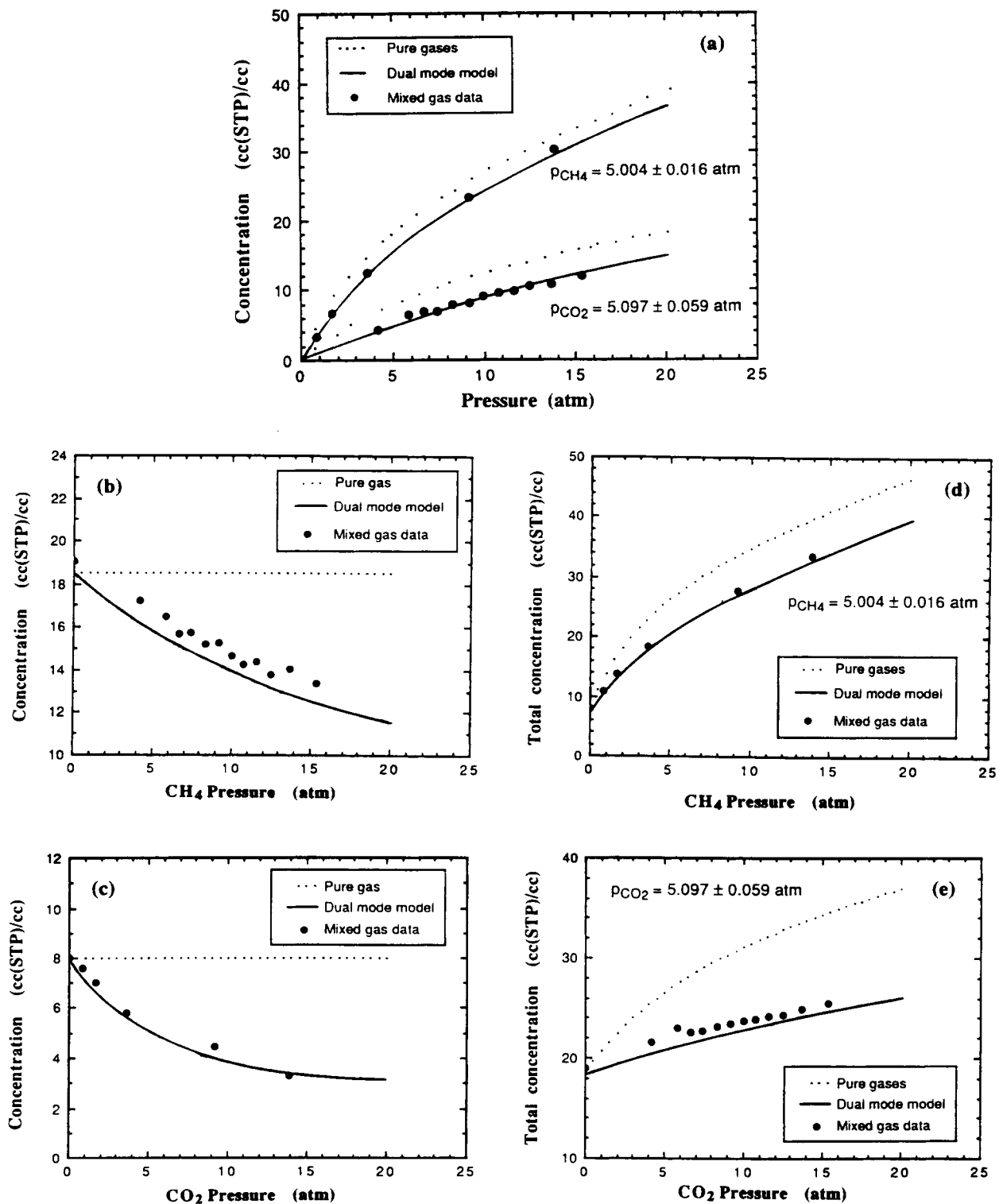
Figure 4 (a) Mixed gas sorption in the PPO/CO₂/CH₄ system; (b) sorption of CO₂ in PPO with increasing CH₄ partial pressure (p_{CO_2} = 5.097 ± 0.059 atm); (c) sorption of CH₄ in PPO with increasing CO₂ partial pressure (p_{CH_4} = 5.004 ± 0.016 atm); (d) total gas sorption in the PPO/CO₂/CH₄ system (constant CH₄ partial pressure); (e) total gas sorption in the PPO/CO₂/CH₄ system (constant CO₂ partial pressure).

illustrate the sorption depression of the gas being maintained at constant partial pressure as a function of increasing pressure of the other gas. Finally, Figures 4(d)–(e) show the total sorption of both gases in each case.

The PPO mixed gas sorption data indicate that the dual mode sorption model, using the parameters shown in Table II, gives a very accurate description of gas mixture sorption. For the $PPO/CO_2/CH_4$ system, for a CO_2 pressure of 20 atm, the model predicts a 4.7% depression in CO_2 sorption in the presence of 5 atm of CH_4, as well as a 63% drop in CH_4 sorption as CO_2 pressure is increased to 20 atm. For the case of CH_4 sorption in the presence of 5 atm of CO_2, the dual mode model predicts a 19.5% depression of CH_4 sorption at 20 atm and a 38% CO_2 sorption decrease as CH_4 pressure is increased to 20 atm. All data points fall practically on top of the model predictions, except for the case of CO_2 during addition of CH_4 shown in Figure 4(b). In the latter case, the data are consistently slightly higher than the model prediction, but only by about 7% at 15 atm CH_4. All other experimental data are centered about the isotherms, and scatter is limited to within ±5% of the theoretical mixed gas isotherms.

Similar results are observed for the $CPPO/CO_2/CH_4$ system. Figures 5(a)–(e) show that all mixed gas data fall along the dual mode model predictions for the case of constant partial pressures of 5 atm, with experimental deviation again no more than 5%. Mixed gas sorption in the $CPPO/CO_2/CH_4$ system was also studied for the case of a constant partial pressure of approximately 10 atm. Using the higher constant partial pressure, CH_4 sorption data are slightly more scattered, but still centered about the predicted mixed gas isotherms, as shown in Figures 6(a)–(e).

It has been reported that the dual mode model predictions of mixed gas sorption can be improved by using fugacity-based sorption parameters.[9,12] These parameters are determined by fitting sorption data as a function of gas fugacity rather than pressure. They can then be used to predict mixed gas sorption as a function of the fugacity of each mixture component. For the present research, the Soave–Redlich–Kwong (SRK) equation of state was used to calculate the fugacity of CO_2 and CH_4 in the gas sorption mixtures. Figures 7(a)–(e) show the mixed gas sorption data for the $PPO/CO_2/CH_4$ system, previously shown in Figure 4, with the pure and mixed gas sorption isotherms recalculated on a fugacity basis. Clearly, the use of fugacity-based data and sorption parameters does not offer a significant

improvement over pressure-based calculations, at least over the range of pressures considered here. Similar comparisons were made between pressure- and fugacity-based calculations for both of the other mixed gas sorption data sets, and no significant improvements were found. Thus, there does not appear to be any advantage in using gas fugacity-based sorption parameters for the prediction of mixed gas behavior for the range of partial pressures studied for PPO and CPPO.

The confirmed accuracy of the dual mode model in predicting mixed gas sorption is important in that it allows the accurate calculation of mixed gas diffusivity. Moreover, it illustrates the use of the mixed gas dual mode sorption theory for medium and high flux polymers which have potential in gas separation applications. We have recently studied several mixed gas permeability models which incorporate the dual mode sorption model for the description of mixed gas solubility. Since the dual mode model accurately predicts the solubility of gas mixtures in PPO and CPPO, any deviations between these mixed gas permeability models and mixed gas permeability data should be attributable to the models' descriptions of the diffusivity of the individual mixture components. This issue is addressed in a recent paper.[1] Finally, the wide range of polymer polarities covered by the three materials in Table I suggests that the use of the mixed gas dual mode sorption model for polymers of any polarity is justified, at least for the CO_2/CH_4 system.

## Numerical Simulation of Experimental Mixed Gas Sorption Technique

As described earlier, the mixed gas sorption technique used in this research involves maintaining the partial pressure of one component constant over the course of the entire experiment. This is accomplished by varying the amount of gas which is removed from the polymer chamber for GC analysis. The size of this gas sample can be chosen such that any gas A which has been displaced from the polymer via competitive sorption with gas B is removed, thus returning the partial pressure of gas A to its value prior to introduction of gas B. Prior to this research, the proper GC sample size for maintaining a constant partial pressure of one gas component was determined by trial and error and experience with the gas/polymer system being studied. However, if the dual mode sorption model is accurate for gas mixtures, the mixed gas sorption expressions can be coupled with the experimental mass balance calculations to predict the exact amount of removed
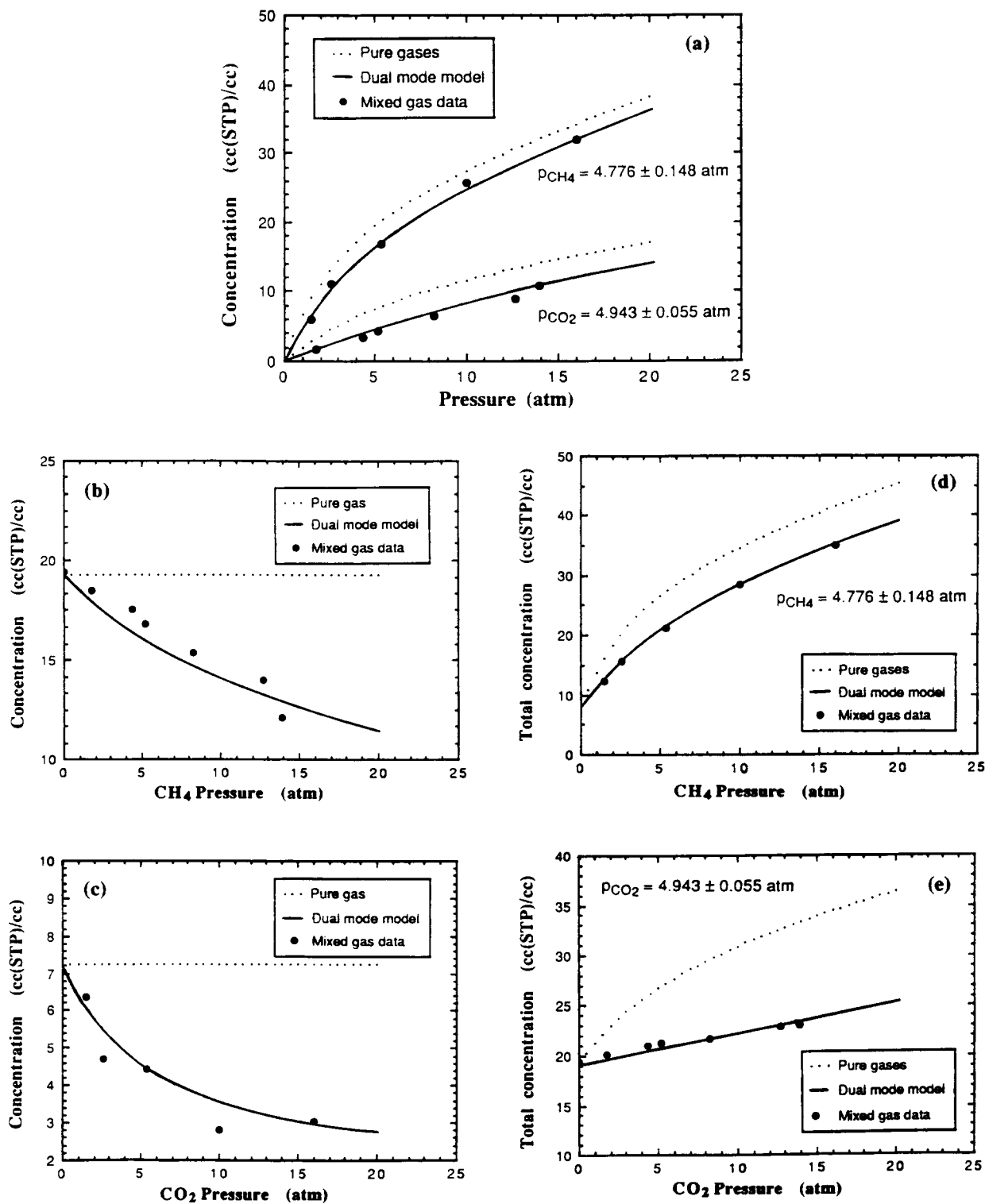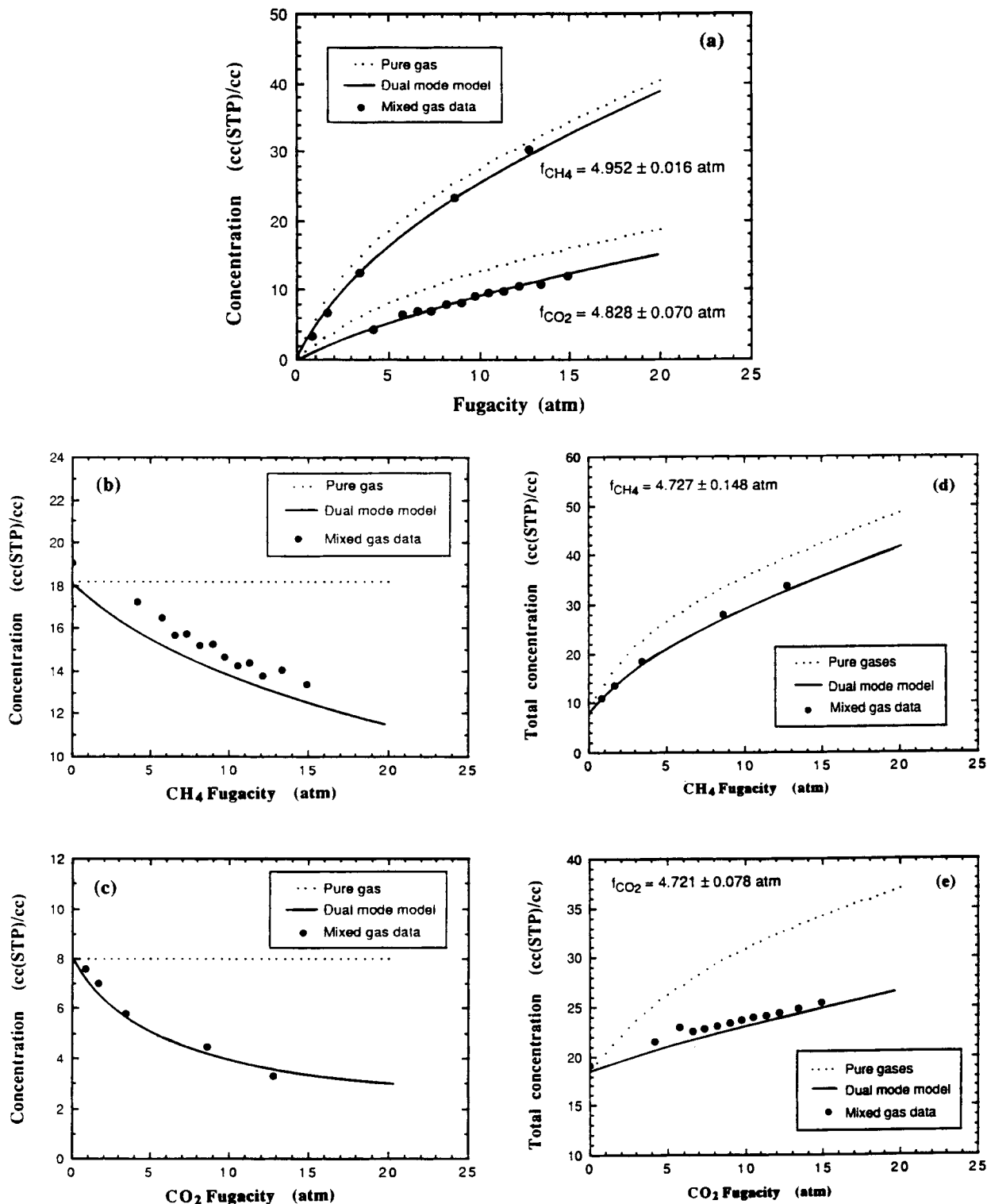
Figure 5   (a) Mixed gas sorption in the CPPO/CO$_2$/CH$_4$ system; (b) sorption of CO$_2$ in CPPO with increasing CH$_4$ partial pressure (p_{CO_2} = 4.943 ± 0.055 atm); (c) sorption of CH$_4$ in CPPO with increasing CO$_2$ partial pressure (p_{CH_4} = 4.776 ± 0.148 atm); (d) total gas sorption in the CPPO/CO$_2$/CH$_4$ system (constant CH$_4$ partial pressure); (e) total gas sorption in the CPPO/CO$_2$/CH$_4$ system (constant CO$_2$ partial pressure).
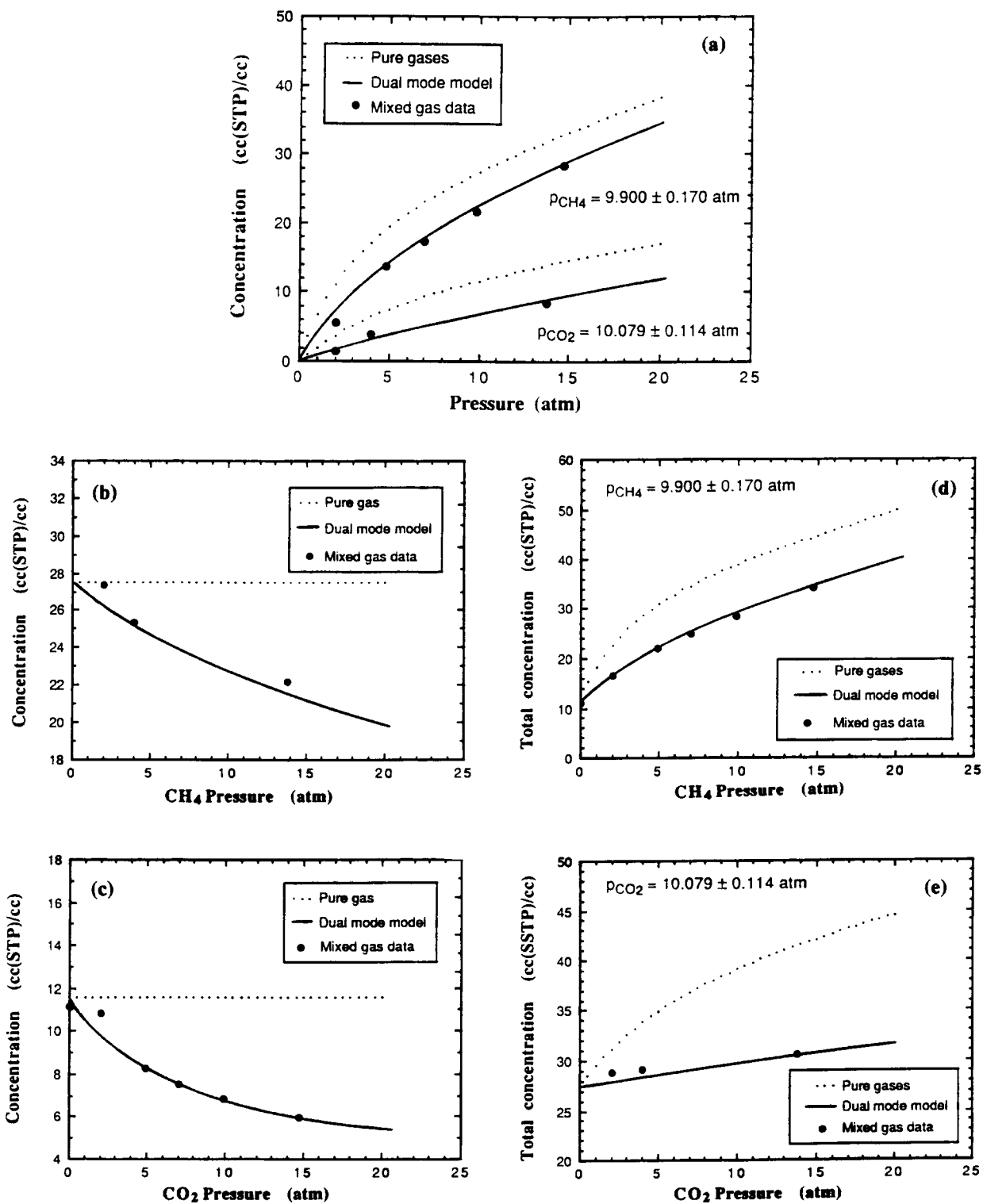
Figure 6 (a) Mixed gas sorption in the CPPO/CO$_2$/CH$_4$ system; (b) sorption of CO$_2$ in CPPO with increasing CH$_4$ partial pressure (p_{CO_2} = 10.079 ± 0.114 atm); (c) sorption of CH$_4$ in CPPO with increasing CO$_2$ partial pressure (p_{CH_4} = 9.900 ± 0.170 atm); (d) total gas sorption in the CPPO/CO$_2$/CH$_4$ system (constant CH$_4$ partial pressure); (e) total gas sorption in the CPPO/CO$_2$/CH$_4$ system (constant CO$_2$ partial pressure).

Figure 7 (a) Mixed gas sorption in the PPO/CO₂/CH₄ system; (b) sorption of CO₂ in PPO with increasing CH₄ partial fugacity (f_{CO_2} = 4.828 ± 0.070 atm); (c) sorption of CH₄ in PPO with increasing CO₂ partial fugacity (f_{CH_4} = 4.952 ± 0.016 atm); (d) total gas sorption in the PPO/CO₂/CH₄ system (constant CH₄ partial fugacity); (e) total gas sorption in the PPO/CO₂/CH₄ system (constant CO₂ partial fugacity).

gas sample which will maintain the desired constant partial pressure of a specified component.

The development of the mixed gas mass balance in terms of the predicted dual mode gas concentrations is presented in the Appendix. The result is a system of equations which can be solved numerically to predict the gas pressure and polymer concentration of each component after the addition or removal of pure or mixed gases from the system. Therefore, the experimental model can be used to predict mixed gas sorption, as in the case of addition of a second gas B to a system of pure gas A, or desorption as in the case of GC sample removal. The computer program MIGAS (Mixed Gas Apparatus Simulator) was written to perform these calculations, and is described in the Appendix. It can be used for three purposes:

(1) prediction of mixed gas sorption after addition or withdrawal of pure or mixed gases from the polymer chamber,

(2) calculation of the amount of gas A added to the polymer chamber which will increase the partial pressure of gas B to a specified value, or

(3) calculation of the amount of gas B added to the polymer chamber which will increase the partial pressure of gas A to a specified value.

MIGAS proved quite useful in maintaining a constant partial pressure of either gas component. The simulator was used to predict the equilibrium sorption of both components after withdrawal of a GC sample, and then to calculate the amount of additional gas required to return the other component's partial pressure to the desired constant value. Sanders reported mixed gas sorption in PMMA for a constant CO_2 partial pressure of 4.45 ± 0.09 atm, for an average partial pressure deviation of 2.02%.[11]

Table III Constant Partial Pressures Maintained in Mixed Gas Sorption Measurements

System	p_{CO_2} (atm)	p_{CH_4} (atm)
PPO/CO_2/CH_4	5.097 ± 0.059 (± 1.15%)	5.004 ± 0.016 (± 0.32%)
CPPO/CO_2/CH_4	4.943 ± 0.055 (± 1.11%)	4.776 ± 0.148 (± 3.10%)
CPPO/CO_2/CH_4	10.079 ± 0.114 (± 1.13%)	9.900 ± 0.170 (± 1.71%)

Table IV Constant Fugacities Maintained in Mixed Gas Sorption Measurements

System	f_{CO_2} (atm)	f_{CH_4} (atm)
PPO/CO_2/CH_4	4.828 ± 0.070 (± 1.45%)	4.952 ± 0.016 (± 0.32%)
CPPO/CO_2/CH_4	4.721 ± 0.078 (± 1.65%)	4.727 ± 0.148 (± 3.13%)
CPPO/CO_2/CH_4	9.386 ± 0.436 (± 4.64%)	9.700 ± 0.166 (± 1.71%)

By comparison, MIGAS was used to maintain the partial pressure of CO_2 in the PPO/CO_2/CH_4 system at 5.097 ± 0.059 for a deviation of 1.15%. It should be noted that the use of MIGAS eliminated the need for "backtracking," which refers to the withdrawal of additional gas samples in order to reestablish the targeted constant partial pressure. Backtracking was a frequent necessity during the early stages of mixed gas sorption measurements, prior to the development of MIGAS. The small deviations in constant partial pressures for all of the mixed gas measurements are given in Tables III and IV.

MIGAS should be especially useful when measuring mixed gas sorption using newly calibrated mixed gas sorption equipment or unfamiliar gas/polymer systems. Much of the guesswork previously required in such situations can be eliminated. The simulator is limited only by the accuracy of pure gas sorption data and dual mode parameters.

CONCLUSIONS

Mixed gas sorption in the PPO/CO_2/CH_4 and CPPO/CO_2/CH_4 systems is predicted accurately by the dual mode sorption model. A constant partial pressure of either 5 or 10 atm of one component was maintained during the experiments. In all cases, sorption isotherms for both components are predicted to within 5% of the mixed gas data. The data from this study effectively bracket the mixed gas CO_2/CH_4 solubility of a wide range of polymers in terms of their overall permeability and selectivity, as well as their chemical character. Any deviations of mixed gas permeability data for these polymers from mixed gas permeability model predictions can thus be attributed to diffusivity factors.

The experimental technique used in mixed gas sorption measurements can be accurately simulated

by assuming dual mode sorption behavior. A computer simulation of the technique predicts the required amounts of pure gases added to the polymer chamber, as well as the required GC sample withdrawal, to achieve a specified constant partial pressure of either gas component. The simulator limits the deviation in this target partial pressure to about 1% and eliminates much of the trial and error technique previously associated with mixed gas sorption measurements.

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APPENDIX: DEVELOPMENT OF THE COUPLED DUAL MODE SORPTION MODEL AND THE MIXED GAS SORPTION MASS BALANCE

The coupled dual mode sorption/mass balance equations will be developed for the general case of addition of a mixture of gases A and B to a polymer in equilibrium with initial partial pressures p_{A1} and p_{B1}. This development assumes that the final concentrations of gases A and B in the polymer, as described by the dual mode sorption model, are equal to the experimentally calculated values:

$$\begin{pmatrix} \text{dual mode sorbed} \\ \text{concentration of gas } i \end{pmatrix}$$
$$= \begin{pmatrix} \text{initial sorbed} \\ \text{concentration of gas } i \end{pmatrix} + \begin{pmatrix} \text{moles of gas } i \\ \text{added to system} \end{pmatrix}$$
$$- \begin{pmatrix} \text{final moles of } i \\ \text{in gas phase} \end{pmatrix}$$

For each component, the equations are written as follows:

$$k_{D_A} p_A + \frac{C'_{H_A} b_A p_A}{1 + b_A p_A + b_B p_B}$$
$$= \left(C_{A1} + \frac{22{,}415}{V_p} n_{A1} + \frac{22{,}415}{V_p} n_{A_{add}} \right)$$
$$- \frac{22{,}415}{V_p} n_A \quad \text{(A.1)}$$

$$k_{D_B} p_B + \frac{C'_{H_B} b_B p_B}{1 + b_A p_A + b_B p_B}$$
$$= \left(C_{B1} + \frac{22{,}415}{V_p} n_{B1} + \frac{22{,}415}{V_p} n_{B_{add}} \right)$$
$$- \frac{22{,}415}{V_p} n_B \quad \text{(A.2)}$$

where C_{A1}, C_{B1}, n_{A1}, and n_{B1} are the initial sorbed concentrations and moles of components A and B in the gas phase, $n_{A_{add}}$ and $n_{B_{add}}$ are the moles of each gas added to the polymer chamber, and p_A, p_B, n_A, and n_B are the final pressures and moles of each component in the gas phase. V_p is the polymer volume, and the conversion factor 22,415 has units of cc(STP)/mol, since the units of sorbed gas concentration are cc(STP)/cc polymer. The n_i terms can be replaced by the following expressions:

$$n_{A1} = \frac{p_{A1}V}{z_m RT} \qquad (A.3)$$

$$n_{B1} = \frac{p_{B1}V}{z_m RT} \qquad (A.4)$$

$$n_{A} = \frac{p_{A}V}{z_m RT} \qquad (A.5)$$

$$n_{B1} = \frac{p_{B}V}{z_m RT} \qquad (A.6)$$

$$n_{A_{add}} = \frac{V_{res}}{RT}\left(\frac{p_{A1_{res}}}{z_{A1_{res}}} - \frac{p_{A2_{res}}}{z_{A2_{res}}}\right) \qquad (A.7)$$

$$n_{B_{add}} = \frac{V_{res}}{RT}\left(\frac{p_{B1_{res}}}{z_{B1_{res}}} - \frac{p_{B2_{res}}}{z_{B2_{res}}}\right) \qquad (A.8)$$

where V is the volume of the gas phase in the polymer chamber, z_m is the compressibility of the mixture calculated using the SRK equation of state, V_{res} is the volume of the reservoir chamber of the sorption cell, $p_{A i_{res}}$, $z_{A_{res}}$, $p_{B i_{res}}$, and $z_{B i_{res}}$ are the pressures and compressibilities, respectively, of each component in the reservoir chamber before and after the addition of each component to the polymer chamber. The determination of mixed gas compressibilities involves a separate numerical solution of the SRK equation of state. The method employed by Sanders was used in this work.[9]

MIGAS solves eqs. (A.1)–(A.8) and the mixed gas compressibility expressions using ZSPOW, a nonlinear equation solver from the IMSL (International Math and Statistics Library). This algorithm uses Powell's method for the solution of a series of nonlinear equations.[18] The required inputs are the initial partial pressure and sorbed concentration of each component, as well as the pressure and composition of any withdrawn GC samples. Initial guesses for each partial pressure must be provided, and it was found that the algorithm converges rapidly if the first guesses are within 1 atm of the correct values.