Sorption and transport mechanism of gases in polycarbonate membranes

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Abstract

The transport phenomena of oxygen and nitrogen across a pure polycarbonate (PC) and a cobalt(III) acetylactonate (Co(acac)$_3$) containing PC membrane was studied. Co(acac)$_3$ was added into a polycarbonate membrane to enhance its oxygen solubility. The oxygen sorption isotherms was measured. It was found that the oxygen solubility decreased sharply as pressure increased, especially at low pressure region. On the contrary, the oxygen permeability increased slightly with respect to pressure. Both the solution–diffusion model and traditional dual mobility model were unable to explain the inconsistent pressure dependency between solubility and permeability. Instead of adopting Langmuir–Henry sorption model, a modified dual mobility model which incorporates BET-type isotherm to describe oxygen sorption. The diffusivity of molecules moving at the first adsorbed layer was assumed to be different from those moving at higher layers. This modified dual mobility model satisfactorily described both the pressure dependency of oxygen solubility and permeability. It was also found that the increase of oxygen/nitrogen selectivity was not due to the elevation of oxygen to nitrogen solubility ratio but due to the mobility ratio of oxygen to nitrogen at the higher adsorption layers.

Keywords: Polycarbonate; Cobalt(III) acetylacetonate; Sorption; Permeability

1. Introduction

Traditionally the behavior of gas transport through a gas separation membrane was presumably dominated by the diffusion of absorbed molecules. The gas flux (j) was driven by the concentration gradient of absorbed molecules in polymer matrix. This leads to a simple model which was known as the solution–diffusion model. The permeability coefficient (p) defined as $p=j/\Delta P$, ΔP being pressure drop, can therefore be expressed as

$$p = D * S$$

where D is the penetrant diffusivity and S is the solubility coefficient.

The gas sorption to a homogenous polymer has been classified into two categories. For sorption to a rubbery polymer membrane, the sorption behavior was described by Henry's law and the sorption isotherm is expressed by $C=S*P$, where C is the concentration of gas absorbed in the polymer at pressure P, and S denotes the solubility coefficient [1]. Recently, a more complex BET-type sorption isotherm which describes multilayer sorption has also been discussed. For sorption to a glassy polymer membrane, the sorption isotherm have been characterized by many authors by a dual mode sorption model, which combines two

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isotherms: a Henry-type isotherm for matrix absorption and a Langmuir-type isotherm for site sorption [2–6].

The gas transport behavior for glassy polymer is then described by a so-called dual mobility model [7,8] which assigns two different diffusivities to molecules absorbed by different mechanisms, Langmuir and Henry's sorption. The dual mobility model is expressed as

$$j = \left[D_m + D_s \frac{QK}{(1 + KP_1)(1 + KP_2)}\right] \Delta P$$

where D_m and D_s denote the matrix diffusivity and the site diffusivity, respectively. This model well described the pressure dependency of gas permeability of a wide range of glassy polymer membrane [9–11] and reasonably related the gas solubility to its permeability. However, this description was successful only when the gas permeability decreased in response to the increase of operating pressure. Houde et al. [12] had observed three different types of pressure dependency of membrane permeabilities: (1) The first type pressure dependency: Gas permeability decreased with increasing ΔP. The permeability of CO_2 through a wide range of polymer membranes, such as polystyrene (PS) or polysulfone (Psf), decreased with respect to the increase of upstream pressure. This type of pressure dependency could be easily described by the dual mobility model. (2) The second type pressure dependency: The permeability increased with the increase of cross-membrane pressure difference, ΔP. When CO_2 diffused through polymethylmethacrylimide (PMMA) or cellulose acetate (CA) membranes, the effect of operating ΔP on gas permeability was totally opposite to that through PS or Psf membranes. (3) The third type pressure dependency was observed when CO_2 diffused through a polycarbonate membrane. The permeability declined with increasing upstream pressure at low pressure region but came back up as the operating pressure further increased. The pressure dependency of the second and third types can no longer be described by the traditional dual mobility model.

We had measured the solubility of oxygen in polycarbonate membranes at different pressures. It was found that the oxygen solubility decreased but the permeability increased slightly with increase of pressure. The addition of an oxygen carrier, $Co(acac)_3$, caused an increase in oxygen solubility, especially at low pressure region. However, it did not lead to an increase in oxygen permeability, neither at low nor at high pressure region. According to the solution–diffusion model or the traditional dual mobility model, permeability and solubility should have the same pressure dependency unless the diffusivities is a strong function of pressure.

The main purpose of this paper is to discuss the relation between gas sorption and permeability, and to explain the transport behavior of the second and the third types. Polycarbonate was known to have good selectivity of oxygen over nitrogen. The mechanism of membrane transport of oxygen and nitrogen has never been carefully studied. In this paper the sorption isotherms and permeabilities of O_2 and N_2 were carefully measured; several possible gas transport models were examined in order to give a reasonable explanation for the transport behavior of oxygen across polycarbonate membranes. A modified dual mobility was proposed to describe the transport mechanism. Multilayer adsorption isotherm was incorporated into the model and two different diffusivities were assigned to the transport of molecules through the first adsorbed layer and the upper layers, respectively. In addition, the traditional solution–diffusion model implies the increase of the solubility of the desired product leads to an increase of its selectivity. But in effect the extent of selectivity improvement varies from system to system. Therefore, we also studied the effect of solubility on oxygen/nitrogen selectivity by varying the oxygen solubility through oxygen carriers addition. These results helped us to analyze the possible mechanisms for gas separation.

1.1. Theory

It is assumed that the gases transport predominantly through the inter-nodule space rather than across polymer nodules. The basic concept is shown graphically in Fig. 1. Both surface diffusion and Knudsen flow are considered. The surface diffusion is driven by the concentration difference of surface adsorption. The pressure dependency of gas adsorption was described by the BET isotherm,

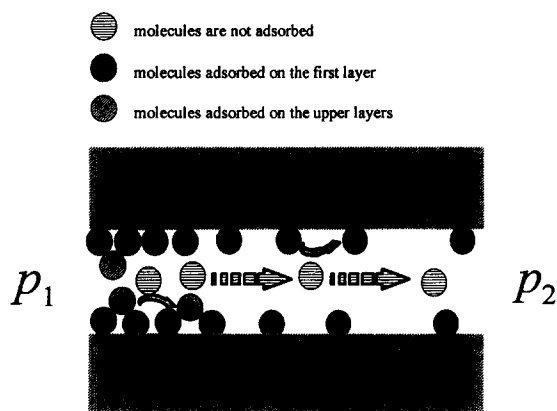$$q = \frac{QcKP}{(1 - KP)(1 - KP + cKP)}$$

Fig. 1. The proposed model of gas transport across a polymeric membrane.

where q denotes the amount of molecules adsorbed, Q represents the amount of molecules forming a monolayer, K is the adsorption constant between adsorbed layers and c denotes the adsorption constant ratio of the first to the upper layers. The BET isotherm can be decomposed into two terms:

$$q = \frac{Q(c-1)KP}{1+(c-1)KP} + \frac{QKP}{1-KP} \quad (1)$$

The first term is actually a Langmuir-type isotherm which accounts for the amount of molecules adsorbed at the first layer. The second term describes the amount of molecules adsorbed at the upper layers. When high affinity carriers are added, part of the first adsorbed layer covers over the surface of the carriers. The above equation can be modified as

$$q = \frac{QKP}{1-KP} + \frac{Q_1(c_1-1)KP}{1+(c_1-1)KP} + \frac{(Q-Q_1)(c_2-1)KP}{1+(c_2-1)KP} \quad (2)$$

where $Q-Q_1$ is the surface capacity provided by the oxygen carriers, c_2K is the adsorption constant between gas molecules and oxygen carriers, and c_1K represents the adsorption constant between polymer and gas molecules. The transport of gas molecules can be described by $j = D_s(\partial q/\partial z)$, where D_s denotes the diffusivity of surface diffusion. When Eq. (1) is used to describe the gas adsorption on a polycarbonate membrane and the downstream pressure P_2 was low,

the gas flux can be reduced to

$$j = \left[D_{s_2} \frac{QK}{1-Kp_1} + D_{s_1} \frac{Q(c-1)K}{1+(c-1)KP_1} \right] \Delta P \quad (3)$$

where D_{s_1} and D_{s_2} are the surface diffusivities of the first and the upper adsorbed layers, respectively. The permeability p $(=j/\Delta P)$ can therefore be expressed as follows:

$$p = D_{s_2} \frac{QK}{1-KP_1} + D_{s_1} \frac{Q(c-1)K}{1+(c-1)KP_1} \quad (4)$$

If oxygen carriers were added to the membrane, the above equation can be modified as

$$p = D_{s_2} \frac{QK}{1-KP_1} + D_{s_1}' \frac{Q_1(c_1-1)K}{1+(c_1-1)KP_1} + D_{s_1}'' \frac{(Q-Q_1)(c_2-1)KP}{1+(c_2-1)KP_1} \quad (5)$$

If oxygen has a very high affinity toward the oxygen carrier, that is, when c_2 is large, Eq. (5) can be reduced to

$$p = D_{s_2} \frac{QK}{1-KP_1} + D_{s_1}' \frac{Q_1(c_1-1)K}{1+(c_1-1)KP_1} + D_{s_1}'' \frac{(Q-Q_1)}{P_1} \quad (6)$$

If there exists Knudsen flow, extra term of Knudsen diffusivity, D_K, is added to the permeability. Eqs. (4) and (6) become

$$p = D_K + D_{s_2} \frac{QK}{1-KP_1} + D_{s_1} \frac{Q(c-1)K}{1+(c-1)KP_1} \quad (7)$$

and

$$p = D_K + D_{s_2} \frac{QK}{1-KP_1} + D_{s_1}' \frac{Q(c_1-1)K}{1+(c_1-1)KP_1} + D_{s_1}'' \frac{Q-Q_1}{P_1} \quad (8)$$

2. Experiment

2.1. Materials

Polycarbonate (Uplion S-2000) ($M_w=28\,000$) was supplied by Mitsubishi. Dichloromethane and cobalt acetylacetonate were supplied by Merck. All above mentioned chemicals are of reagent grade and without further purification.

2.2. Membrane preparation

The PC membrane was prepared from a casting solution of polycarbonate in dichloromethane. The membranes was formed by casting the solution onto a glass plate to a predetermined thickness using a Gardner knife at room temperature. The membrane dried in vacuum for 24 h before gas sorption and permeation measurement. When the cobalt acetyl acetonate content was over 30 wt%, precipitation of the salt occurred leading to poor membrane formation.

2.3. Gas permeability measurements

The apparatus (Yanaco Gas Permeability Analyzer, model GTR-10) for measuring the permeability of gas through the membrane is showing as our previous report [13]. The gas permeability was measured by the following equation:

$$p = \frac{l}{(P_1 - P_2)} \frac{q/t}{A}$$

where p is the gas permeability [cm^3(STP) cm/ cm^2 s cmHg], q/t is the volume flow rate of gas permeate [cm^3(STP)/s], l is the thickness [cm], P_1 and P_2 are the pressures (cmHg) on the high pressure and low pressure side of the membrane respectively, and A is the effective membrane area [cm^2].

2.4. Gas sorption measurements

The experimental setup for gas sorption measurement is shown as our previous report [14]. A microbalance (Cahn Model D-202 Electrobalance) was enclosed in a stainless chamber. The chamber was enclosed in a constant temperature Box. The system pressure was then vacuumed to about 4×10^{-3} torr before the gas sorption measurement. The system was under the condition until sorption equilibrium was reached.

3. Results and discussion

3.1. The pressure dependency of oxygen solubility and permeability of polycarbonate membrane

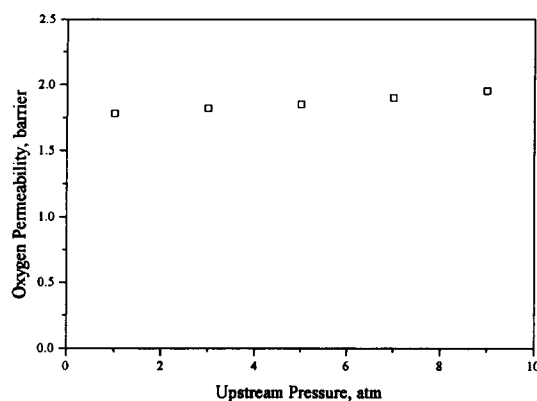The effect of operating upstream pressure on oxygen permeability was examined and the data is pre-

Fig. 2. The pressure dependency of oxygen permeation through a PC membrane.

sented in Fig. 2. It was found that the oxygen permeability increased slightly along with the increase of upstream pressure. This type of pressure dependency can be described by the solution–diffusion model if the solubility of oxygen had the same pressure dependency. However, after the sorption isotherm was measured and the solubility was calculated, it was found that the solubility actually decreased with the increase of pressure, which is shown in Fig. 3. The inconsistent pressure dependency of oxygen solubility and permeability makes it difficult to explain the oxygen transport mechanism by the solution–diffusion model.
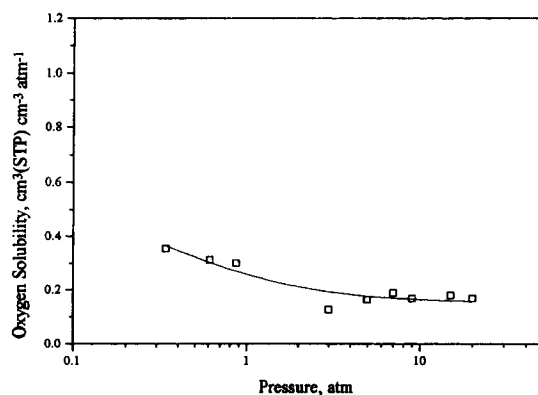
Fig. 3. The pressure dependency of oxygen solubility in a PC membrane. The solid line is the simulation of Langmuir-linear sorption model.
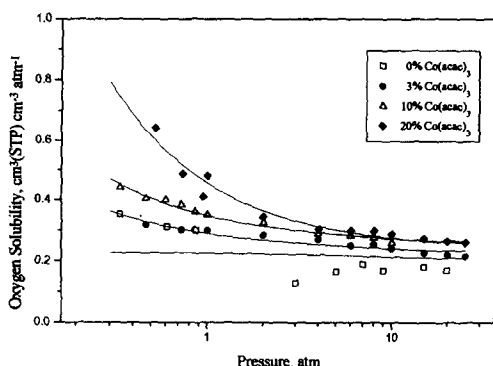
Fig. 4. The pressure dependency of oxygen solubilities in the Co(acac)3 containing PC membranes. The solid lines are values calculated from Eq. (2).
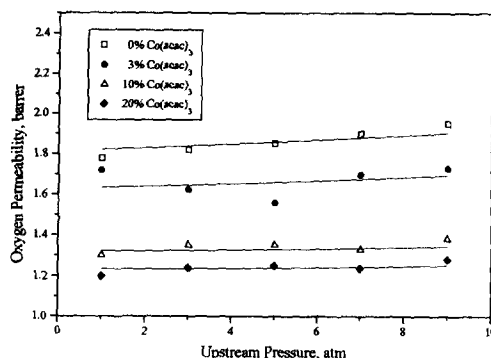

Fig. 5. The pressure dependency of oxygen permeation through the Co(acac)3 containing PC membranes. The solid lines are calculated from the proposed model.

Although the oxygen and nitrogen sorption isotherms of the polycarbonate membrane can be nicely fitted by the dual mode sorption model (the solid line in Fig. 3), it was still difficult to describe the transport mechanism by the traditional dual mobility model. As mentioned above the oxygen permeability increased but the solubility decreased with respect to the increase in pressure. The permeability can hardly be fitted by the dual mobility model even when the diffusivity of Langmuir sorption portion is set zero. Just like the solution–diffusion model, the dual mobility model can only describe the first type pressure dependency of permeability if the gas sorption isotherm follows Langmuir–Henry dual mode sorption model.

In order to avoid being misled by inaccurate measurement, an oxygen carrier Co(acac)3 was added to the PC membrane to increase the oxygen solubility. Both the permeability and the solubility of oxygen were measured. As shown in Fig. 4, the Langmuir sorption apparently increased after the addition of Co(acac)3 and the increase was proportional to the amount of Co(acac)3 added. Therefore, the oxygen solubility sharply decreased with the raise of pressure. However, the pressure dependency of solubility had little effect on that of oxygen permeability. As shown in Fig. 5, the oxygen permeability was almost independent of the operating pressure. The pressure dependency of permeability clearly did not consist with that of gas solubility. Neither the solution–diffusion model nor the dual mobility model is able to explain this discrepancy.

3.2. Describing gas solubility by BET isotherm

Instead of using dual mode sorption model, we adopted BET isotherm to describe oxygen solubility. The solubility of oxygen in polycarbonate membrane could be described by Eq. (1) and the solubility of oxygen in Co(acac)3 containing membrane could be simulated by Eq. (2). As shown in Fig. 4, the solubility data were simulated very well by the BET isotherm. The fitted parameters, Q, K, Q_1, c_1 and c_2 are listed in Table 1. The advantage of using BET isotherm is that the part of solubility introduced by molecules adsorbed at higher layers increases with increasing upstream pressure. As shown in Fig. 6, the solid line represented the part of solubility contributed by the upper layer adsorption. Unlike the first layer adsorption, the solubility contributed by upper layers increased with pressure. By adopting this expression for solubility, the permeability can be expressed by Eqs. (7) and (8) for pure and Co(acac)3 containing polycarbonate membranes, respectively. The solid line shown in Fig. 5 was the model simulation and the symbols were the measured oxygen permeabilities. Table 2 listed the fitted oxygen diffusivities. The model satisfactorily simulated the permeability data and related solubility and permeability nicely. Although this model looked complicated, it simply suggested that as the operational pressure increased, the permeability would decrease if the diffusion was mostly contributed by the molecules adsorbed on the first layer. On the other hand, the permeability would increase if the diffusion was con-

Table 1
Parameters in Eq. (2) to describe the oxygen solubilities

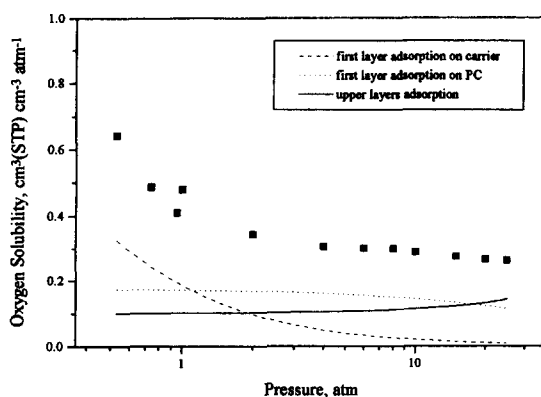| Co(acac)$_3$ content	Q cm^3(STP)/cm^2	Q_1 cm^3(STP)/cm^2	K atm^{-1}	c_1	c_2
0 wt%	6.79	6.79	0.012	2.8	—
3 wt%	7.54	7.50	0.012	2.8	1000
10 wt%	8.53	8.46	0.012	2.8	1000
20 wt%	8.06	8.26	0.012	2.8	1000

Fig. 6. The contribution of each term in Eq. (2) to the oxygen solubilities. The symbols are the measured oxygen solubilities in the 20% Co(acac)$_3$ containing membrane.

tributed by the molecules adsorbed on the upper layers.

3.3. Selectivity was not dominated by the solubility difference between oxygen and nitrogen

Traditionally the increase of solubility was believed to increase the membrane selectivity of the desired product. This belief may originated from either solu-

tion–diffusion or dual mobility model. It led to numerous studies of the selectivity improvement by carrier addition. The addition of Co(acac)$_3$ to facilitate oxygen/nitrogen separation by PC membranes was also stimulated by this belief. The selectivity was indeed improved. As can be seen in Fig. 7(a), the oxygen selectivity increased as more and more Co(acac)$_3$ were added. However, when the O$_2$/N$_2$ solubility ratio shown in Fig. 7(b) was compared with the selectivity shown in Fig. 7(a), we found it difficult to attribute the separation improvement totally to the increase of solubility ratio. Instead, according to the fitted parameters listed in Table 2, the diffusion of oxygen molecules on the first adsorbed layer was much slower than those moving on the higher layers. It was suspected that the O$_2$/N$_2$ selectivity was mainly contributed by the ratio of O$_2$/N$_2$ diffusion rate on the higher sorption layers.

3.4. Mechanism for gas separation suggested by the proposed model

Neither solution–diffusion model nor dual mobility model take Knudsen flow into consideration. To neglect the Knudsen flow, the diffusivities in the solution–diffusion or the dual mobility model have to be a function of both the pore size (the inter-nodule

Table 2
Fitted diffusivities in the proposed model

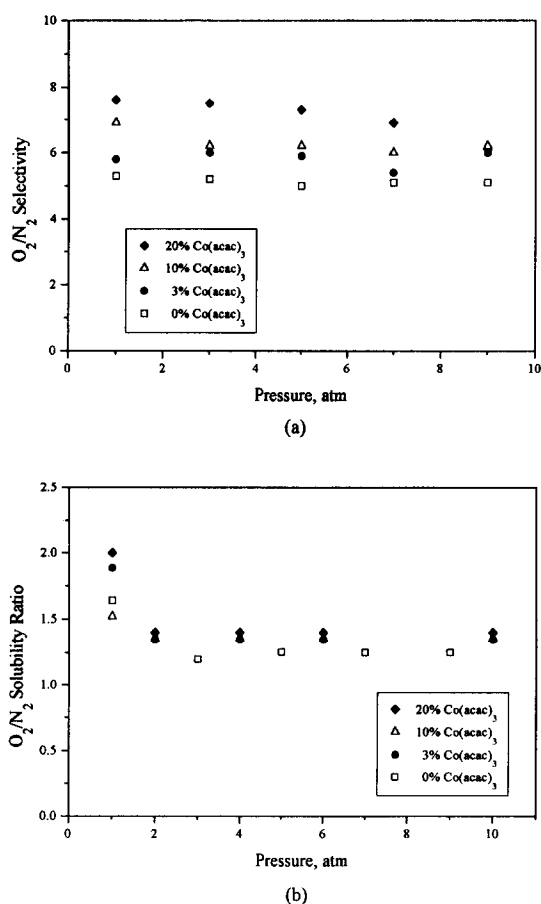| Co(acac)$_3$ content	D_K cm^3(STP) cm/cm^2 s cmHg	D_{S_2}	$D_{S_1}{}'$	$D_{S_1}{}''$
0 wt%	0.279	14.65	2.34	0.0001
3 wt%	0.190	11.64	2.42	0.0001
10 wt%	0.084	7.71	2.46	0.0001
20 wt%	0.042	7.46	2.61	0.0001

Fig. 7. The effect of Co(acac)$_3$ content on the oxygen/nitrogen (a) selectivity and (b) solubility ratio at various pressures.

tacting surface. The Knudsen diffusivity accounts mainly for the effect of pore size reduction caused by Co(acac)$_3$ addition.

The existence of Knudsen flow eases the explanation for membrane transport. Since oxygen and nitrogen have similar molecular weights, little separation can be achieved by Knudsen flow. If the ratio of surface diffusivities through the higher sorption layers is the dominating factor for O$_2$/N$_2$ separation, the existence of nonselective Knudsen flow reduces the selectivity. The addition of Co(acac)$_3$ has two effects: (1) it narrows the inter-nodule space to reduce the nonselective Knudsen flow, and (2) it provides higher sorption capacity to increase the selective surface flow. Consequently, after the addition of Co(acac)$_3$ both the permeability of O$_2$ and N$_2$ decreases because of the reduction in Knudsen flow, but it also leads to the increase of O$_2$/N$_2$ selectivity because the relative portion of selective surface flow increases.

4. Conclusion

Possible mechanisms of oxygen and nitrogen transport through membranes made of pure polycarbonate and polycarbonate containing Co(acac)$_3$ were examined. Both the solution–diffusion model and traditional dual mobility model were not able to explain the inconsistent pressure dependency between solubility and permeability. Instead of adopting Langmuir–Henry dual mode sorption model, it was found that applying BET sorption isotherm to the dual mobility transport model satisfactorily described both the pressure dependency of solubility and permeability. An important point is that the solubility ratio of oxygen to nitrogen was found to contribute only small part of the O$_2$/N$_2$ selectivity. It may be the ratio of surface diffusivities through the higher sorption layers dominating O$_2$/N$_2$ separation. From the experimental data, the proposed model suggests that (1) the selectivity enhancement for oxygen by narrowing the membrane pore size is not accomplished by size selection but by the reduction of nonselective Knudsen flow, and (2) the selectivity enhancement by adding oxygen carriers is not achieved by raising the O$_2$/N$_2$ solubility ratio but by increasing the ratio of surface diffusion to Knudsen flow.

space) and the gas concentration (partial pressures of gases). Consequently the addition of a high affinity carrier usually affects both the gas diffusivity and solubility. One can never tell whether the improvement of membrane selectivity is resulted from the increase of oxygen solubility or from the reduction in membrane pore size. In the proposed model, we introduced Knudsen diffusivity to keep the diffusivities in front of gas sorption terms less affected by either the pore size or the partial pressures of gases. Therefore, the addition of Co(acac)$_3$ affected only those parameters describing gas sorption, i.e. Q_2, c_2K and $Q-Q_1$, which could be obtained from the sorption isotherm. D_{s_1}' and D_{s_1}'' are only functions of the affinity between oxygen molecules and their con-

Acknowledgements

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