

# Dielectric study on membrane adsorption and release: Relaxation mechanism and diffusion dynamics

LI YuHong<sup>1</sup>, ZHAO KongShuang<sup>2†</sup> & HAN Ying<sup>2</sup>

<sup>1</sup>Jiangsu Laboratory of Advanced Functional Materials, Department of Chemistry and Material Engineering, Changshu Institute of Technology, Changshu 215500, China;

<sup>2</sup>College of Chemistry, Beijing Normal University, Beijing 100875, China

**Dielectric monitoring of the adsorption or release process of salicylic acid (SA) by chitosan membrane shows that the dielectric spectra of the chitosan membrane/ SA solution systems change regularly in the adsorption or release process. By analyzing the regularity, a new mechanism for the relaxations is proposed. The concentration polarization layer (CPL) caused by SA adsorption or release is confirmed to be essential for the dielectric relaxations. The changes of the spectra with time are explained by account of the relationship between CPL properties and dielectric strength. Based on this relaxation mechanism, a theoretical method can be established to calculate dynamical parameters of inner structure of the adsorption or release systems from their dielectric spectra. Therefore, dielectric spectroscopy is demonstrated to be a promising method for estimating interfacial distribution of ionic substances and their binding to membrane in a non-invasive way.**

dielectric spectroscopy, concentration polarization, simulation, chitosan, adsorption, release

Chitosan, a natural macromolecule with unique biocompatibility and adsorption property, is widely used in medical, agricultural and biological fields<sup>[1–3]</sup>. The related adsorption theory and controlled-release technology have been the topics of great interest. Of the two, the former focuses on mechanism of interactions between chitosan and adsorbates, while the latter deals with how to monitor adsorption or release processes *in situ*. Many methods have been used in the study of adsorption by chitosan membrane<sup>[4–6]</sup>. However, in most of the methods, samples must be removed from the systems for individual test, so information obtained from these methods does not reflect the real-time situation of the systems.

Dielectric Spectroscopy (DS), a non-invasive method used for detecting electrical, structural and dynamical characteristics of material systems, has been applied in the study of membrane systems by a few research groups, including ours<sup>[7–12]</sup>. Under an AC electrical field, the frequency response of a heterogeneous system con-

taining adsorbate and adsorbent varies due to distribution of the adsorbate. Time dependence of the response signal, i.e. capacitance and conductance of the systems, can be monitored, to obtain information on dynamic changes within the systems. Furthermore, samples is not necessary to be removed from the systems for dielectric measurement, thus the real-time information is obtained. Therefore, DS is a promising method to be applied in practical industry and environmental monitoring. In recent years, the automation of instruments makes it possible for monitoring dynamic process with DS. So far, this technology is mainly applied in monitoring biological cell cultivation, polymer curing and chemical reactions<sup>[13–16]</sup>, but the dielectric monitoring of adsorption or release process has seldom been reported. In fact, the

Received September 15, 2007; accepted September 29, 2007  
doi: 10.1007/s11426-008-0037-0

†Corresponding author (email: zhaoks@bnu.edu.cn)

Supported by the National Natural Science Foundation of China (Grant No. 20673014) and Open Topic Research Foundation of Jiangsu Laboratory of Advanced Functional Materials (No. 06KFJJ009)

key to the success in dielectric monitoring of these processes is the determination of a correct mechanism of the dielectric response, and the establishment of analyzing method for the dielectric spectra. In a previous study, we hypothesized a relaxation mechanism for the adsorption of salicylic acid by chitosan membrane<sup>[9]</sup>. With the deepening of research, this mechanism is insufficient to explain the newly discovered relaxation phenomena. So it is necessary to develop a new mechanism through combining experimental phenomena and relevant dielectric theory.

In this study, DS is used to monitor the processes of adsorption and release of salicylic acid (SA) by chitosan membrane. Through analyzing the influence of adsorption time, acid concentration and thickness of the membrane on the dielectric spectra, the relaxation mechanism related to the dielectric behavior is determined. This provides a theoretical basis for the establishment of a numerical method to analyze the spectra, and ultimately applying DS in monitoring practical drug release processes. In addition, the dynamic parameters obtained by dielectric measurements may also be used for studying interactions between species in the adsorption or release processes.

## 1 Experiment

Chitosan powder, deacetylation of 88.63%, average molecular weight of about  $10^6$ , was provided by Zhejiang Jinke Biochemistry Limited. Other chemicals are analytical reagents. The chitosan membranes were prepared according to ref. [9]. By controlling the concentration of chitosan, two membrane samples with different thickness, called thick membrane (about 80  $\mu\text{m}$ ) and thin membrane (about 8  $\mu\text{m}$ ) below, were prepared. To remove acid introduced in the preparation, the prepared membranes were soaked in distilled water and washed repeatedly.

In a cylindrical cell, chitosan membrane (for adsorption processes) or membrane with adsorbed SA (for release processes) was put parallel to two platinum electrodes at each end of the cylinder, and the two compartments with same volume on both sides of the membrane were filled with SA solution of the same concentration (for adsorption processes) or distilled water (for release processes). Each of the electrodes, as well as the membrane, has an area  $A$  of 3.14  $\text{cm}^2$ . The cell constant, i.e. ratio of the area of each electrode to the distance be-

tween the two electrodes, is 2.414 cm. For experimental details please refer to ref. [17]. Dielectric spectra of the cell system were recorded in the frequency range from 40 Hz to 4 MHz every 5 minutes by an Agilent 4294A precision impedance analyzer controlled by a computer. The voltage of the AC electrical field was 100 mV. All dielectric measurements were carried out at  $20 \pm 1^\circ\text{C}$ . To avoid the swelling of the chitosan membrane during the experiment, very dilute acid solutions were used.

## 2 Results and discussion

### 2.1 Effect of membrane thickness and acid concentration on the relaxation behavior

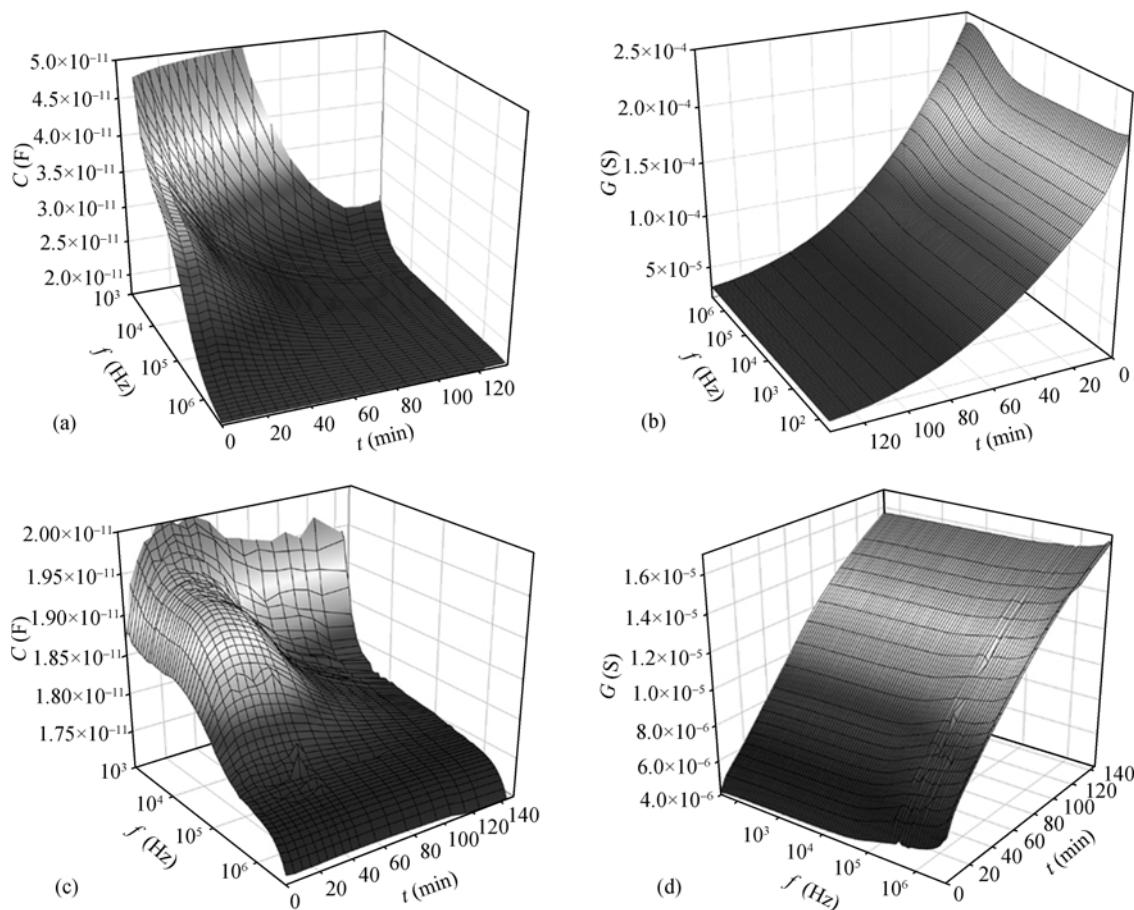
Chitosan membrane of two different thickness in the presence of SA solution of various concentrations show obvious dielectric response, except in two cases, as summarized in Table 1. As an example, Figure 1 shows the dielectric spectra of the adsorption process on the thick membrane (the initial concentration of SA is 0.4  $\text{mmol} \cdot \text{L}^{-1}$ ) and the spectra of subsequent release process. Most of the time, remarkable dielectric relaxations are observed, that is, the measured capacitance  $C$  increases and conductance  $G$  decreases at the same frequency (about  $10^5$  Hz). As the abrupt increase in capacitance at frequency ( $f$ ) below  $10^4$  Hz is believed to be caused by electrode polarization, not the property of the system itself<sup>[18,19]</sup>, the data are not analyzed in this study. The strength of the dielectric relaxations increases in a short period of time and then decreases. Meanwhile, the conductance gradually decreases (for adsorption process) or increases (for release process), showing the progression of the adsorption or release processes. After about 120 min, the relaxation no longer exists, as capacitance (or conductance) does not decrease (or increase) at the frequency around  $10^5$  Hz; moreover, both capacitance and conductance donot change with time, indicative of the completion of the adsorption or release process. In short, during adsorption or release process, the relaxation can be observed, and when the adsorption or release process finish, the relaxation disappear. So the relaxation is an indicator of whether the adsorption or release process is going or finished.

It is interesting to note that in contrast to most of the case, no relaxation is found for the release process of SA from the thick membrane after its adsorbing in 0.1  $\text{mmol} \cdot \text{L}^{-1}$  SA solution. An intuitive explanation is that

**Table 1** Status of dielectric response of each system

Thick membrane (about 80 $\mu\text{m}$ )			Thin membrane (about 8 $\mu\text{m}$ )		
[SA] ( $\text{mmol} \cdot \text{L}^{-1}$ )	existence of relaxation		[SA] ( $\text{mmol} \cdot \text{L}^{-1}$ )	existence of relaxation	
	Ads <sup>a)</sup>	Rel		Ads	Rel
0.10	Yes	No	0.06	Yes	Yes
0.20	Yes	Yes	0.08	Yes	Yes
0.40	Yes	Yes	0.10	Yes	Yes
0.60	Yes	Yes	0.12	Yes	Yes
			0.20	Not obvious	Yes

a) "Ads" refers to adsorption processes. The membrane that has adsorbed SA in the adsorption process is used in the following release process, which is denoted by "Rel" in the table.



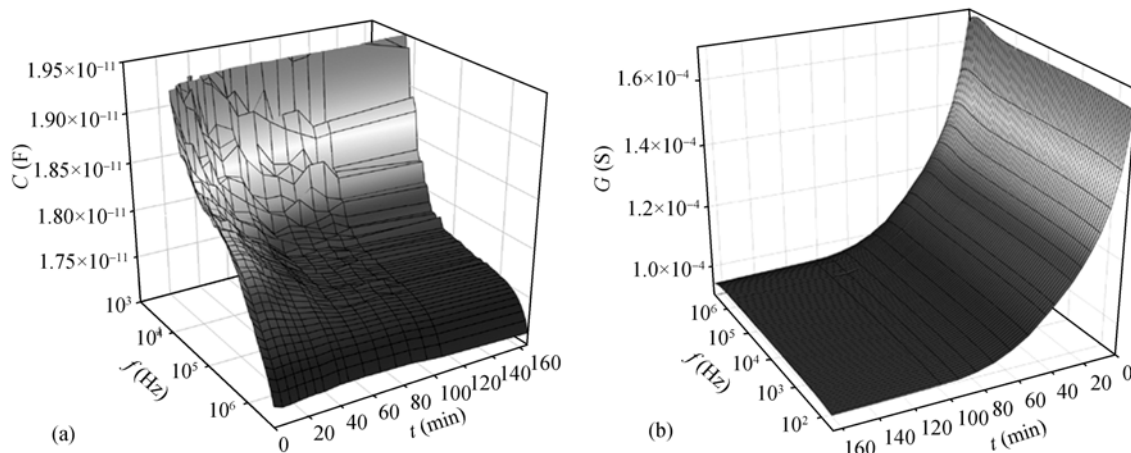
**Figure 1** Dielectric spectra of one of the adsorption processes of the thick membrane ((a) Capacitance  $C$ ; (b) conductance  $G$ , depending on time  $t$  and frequency  $f$ ), and the spectra of the subsequent release process ((c) and (d)). The initial concentration of SA in this adsorption process is  $0.4 \text{ mmol} \cdot \text{L}^{-1}$ .

there is very little acid released from the membrane due to the low adsorbed amount in adsorption process at lower SA concentration and the strong interactions between the adsorbed SA and the chitosan membrane. However, another fact is that no obvious relaxation is found in Figure 2 for the adsorption process of the thin membrane in SA solution of  $0.2 \text{ mmol} \cdot \text{L}^{-1}$ , which contradicts the explanation. As shown in Figure 2, the adsorption did occur in this case as the conductance  $G$  of the system is found to decline with time  $t$  (in Figure 2

(b)), but the relaxation in the spectrum is not pronounced. To find out the reason for this contradiction, it is necessary to investigate the mechanism of the relaxation.

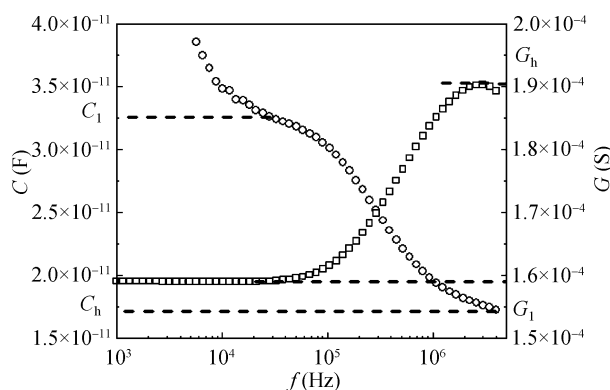
## 2.2 Determination and analysis of dielectric parameters

In order to fully understand the effects of time, concentration of SA and thickness of the membrane on dielectric spectra of the adsorption or release processes, some characteristic parameters should be obtained from the



**Figure 2** Dielectric spectra of one of the adsorption processes of the thin membrane. The initial concentration of SA is  $0.2 \text{ mmol} \cdot \text{L}^{-1}$ . (a) Capacitance  $C$ ; (b) conductance  $G$ .

spectra. How these parameters are obtained is shown schematically in Figure 3. These parameters are: capacitance at low and high frequency limits,  $C_l$  and  $C_h$ , conductance at low and high frequency limits,  $G_l$  and  $G_h$ , and relaxation strength of capacitance  $\Delta C (=C_l - C_h)$  and conductance  $\Delta G (=G_h - G_l)$ .



**Figure 3** Determination of characteristic dielectric parameters in the spectrum.

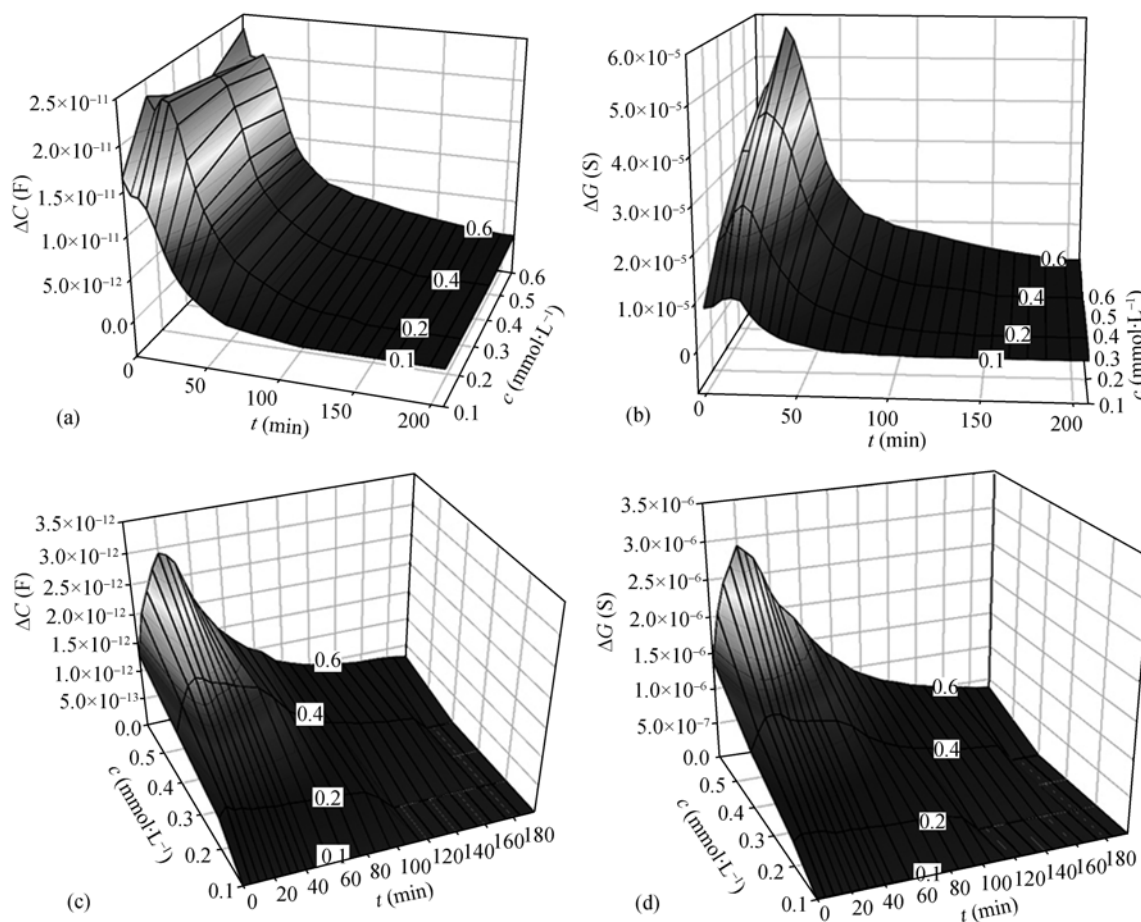
Shown in Figures 4 and 5 are the relaxation strength ( $\Delta C$  and  $\Delta G$ ) changing with time for each situation. As can be seen,  $\Delta C$  and  $\Delta G$  in three types of processes, namely adsorption and release process from thick membrane (Figure 4) and release process from thin membrane (Figure 5(c), (d)), are similar. In these processes,  $\Delta C$  and  $\Delta G$  always increase and are peaked, and afterwards, gradually decrease, fall back to 0, except that there's no relaxation found in the release process of the thick membrane after having adsorbed SA of  $0.1 \text{ mmol} \cdot \text{L}^{-1}$ . Furthermore, at a given time  $t$ , greater re-

laxation strength is observed for the system at larger SA concentration.

On the other hand, the relaxation phenomena for the release process from the thin membrane (Figure 5(a), (b)) are different from those of the other three types of processes. Specifically, there is no peak in the curves of  $\Delta C$  and  $\Delta G$  vs.  $t$ , and  $\Delta C$  and  $\Delta G$  donot increase monotonically with SA concentration. Instead, the relaxation strength reaches maximum at SA concentration of  $0.10 \text{ mmol} \cdot \text{L}^{-1}$ ; and at SA concentration of  $0.20 \text{ mmol} \cdot \text{L}^{-1}$ , the relaxation is no longer observable (see Figure 2).

### 2.3 Validation of the relaxation mechanism

**2.3.1 Possible mechanism.** According to Maxwell-Wagner theory<sup>[20,21]</sup>, for a heterogeneous system with several phases of different conductivity  $\kappa$  and permittivity  $\varepsilon$ , if the condition  $\varepsilon_1/\kappa_1 \neq \varepsilon_2/\kappa_2 \neq \dots \neq \varepsilon_n/\kappa_n$  is satisfied,  $n - 1$  relaxation processes with different characteristic relaxation times will be observed. Based on this principle, the relaxations in this study may arise from electrical property difference between the membrane and the solution. In other words, the expression  $\varepsilon_m/\kappa_m \neq \varepsilon_w/\kappa_w$  is satisfied, where subscripts m and w denote chitosan membrane and the solution, respectively. The changes of the dielectric spectra with time  $t$  may arise from the changes of  $\varepsilon_m$ ,  $\kappa_m$ ,  $\varepsilon_w$  and  $\kappa_w$ , caused by the adsorption or release of SA. Therefore, when the adsorption or release process stops, the relaxation phenomenon should still be observed because the difference in  $\varepsilon$  and  $\kappa$  between the membrane and the solution is still present. However, contrary to the contention, the relaxation disappears when the adsorption or release process stops.



**Figure 4** Time ( $t$ ) and SA concentration ( $c$ ) dependence of the relaxation strength of the adsorption processes ((a)  $\Delta C$ ; (b)  $\Delta G$ ) and the release processes ((c) and (d)), by the thick membrane.

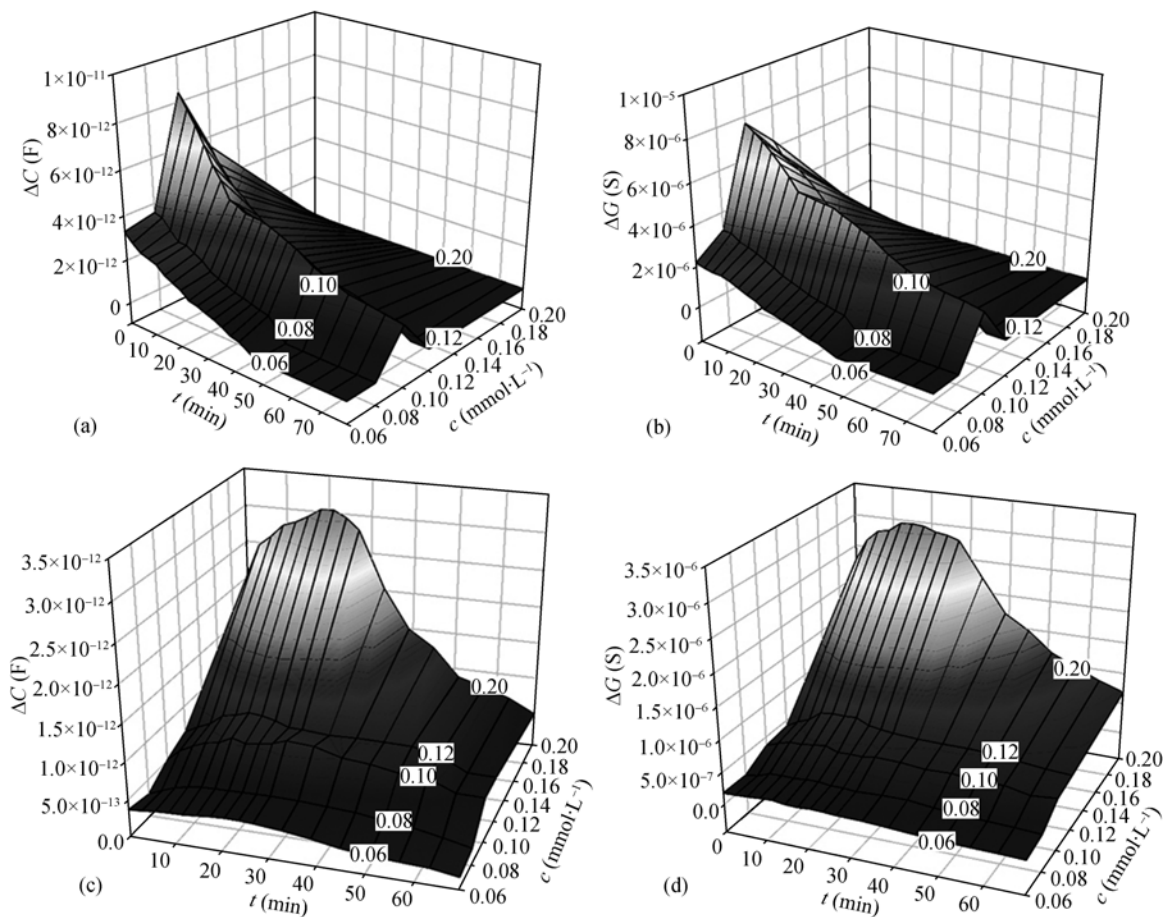
Therefore, the relaxations of current systems are not simply caused by the bulk electrical property difference between the membrane and the solution.

In literatures, most of the membranes showing dielectric relaxations in membrane/solution systems are dense materials with small-scale pores, such as polystyrene membrane, nanofiltration and reverse osmosis membranes. No dielectric relaxation is observed for the system comprising membrane with good permeability and large-scale pores<sup>[22,23]</sup>. In this study, the chitosan membrane is highly hydrophilic due to the existence of free hydrophilic groups such as —OH and —NH<sub>2</sub> on the macromolecule. Upon immersion in water, the membranes are filled with water at the molecular level. Therefore there is little difference between the membrane and the solution in their permittivity  $\epsilon$  and conductivity  $\kappa$ . As a result, the dielectric relaxation is too small to be detected. To prove the contention, we measured the dielectric spectra of membrane/distilled water and that of distilled water alone as shown in Figure 6. There is no

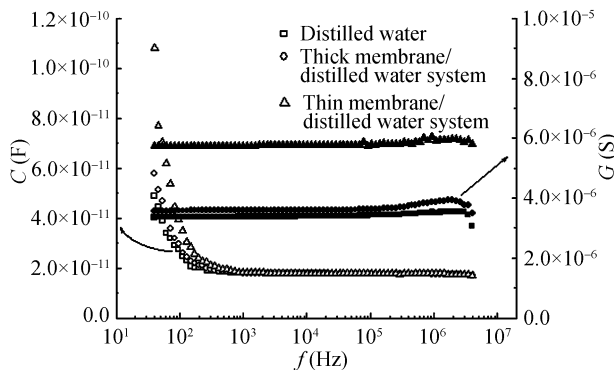
characteristic difference in spectra from both cases except that the former exhibits a slightly higher conductivity (probably due to the trace acid—that had not been thoroughly washed—released from the membrane).

Since the dielectric relaxation does not originate from the bulk electrical property difference between the membrane and the solution, we will discuss what causes the relaxations. Previous studies<sup>[23,24]</sup> revealed that the solution/ion-exchange membrane system, because of high ion permeability of the membrane, did not exhibit relaxation. However, when a DC bias voltage was applied, which caused two concentration polarization layers (CPL) in solutions on both sides of the membrane, dielectric relaxations occurred. In the present study, the adsorption or release of SA also results in the formation of CPLs. It appears the existence of the CPLs causes the dielectric relaxation here. In the absorption or release process, the conductivity gradient and thickness of the CPL change over time and so does the dielectric spectrum. When the adsorption or release process stops, the





**Figure 5** Time ( $t$ ) and SA concentration ( $c$ ) dependence of the relaxation strength of the adsorption processes ((a)  $\Delta C$ , (b)  $\Delta G$ ) and the release processes ((c) and (d)), by the thin membrane.



**Figure 6** Dielectric spectra of thick (or thin) membrane/ distilled water system, compared with that of distilled water in the same measurement cell.

CPL gradually disappears, so no relaxation exhibits. Based on above discussion, the formation of CPL is very likely the main reason for the emerging of dielectric relaxations in this study.

**2.3.2 Dielectric simulation of the CPL.** To further confirm the above inference, it is necessary to correlate

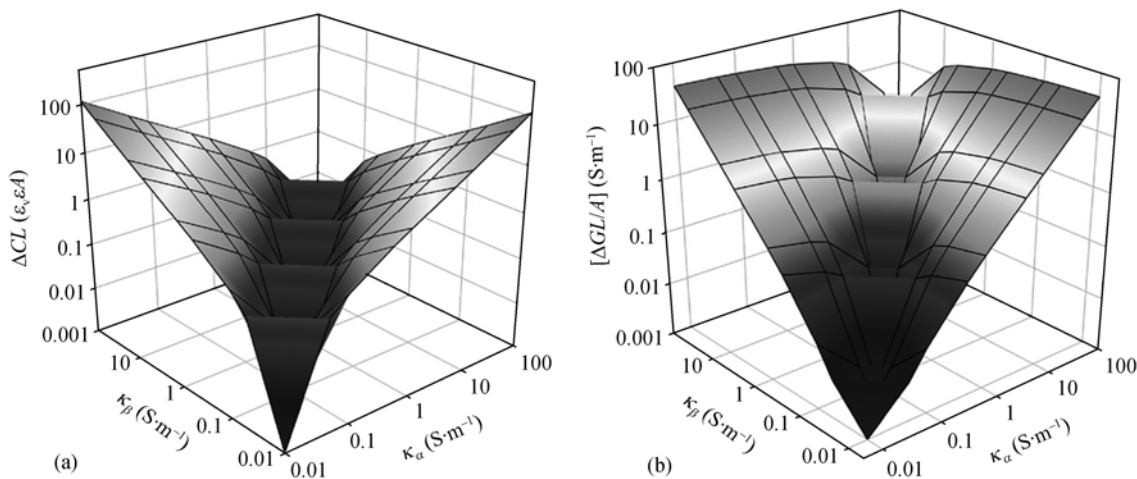
property of the CPL with characteristic of the dielectric spectra. Referring to one of the authors' previous publications<sup>[24]</sup>, expressions of relaxation strength of the CPL, in which the dielectric constant  $\varepsilon$  is assumed to be uniform and the conductivity  $\kappa$  is assumed to be linearly distributed, are derived:

$$\Delta C = \left[ \frac{1}{\xi} \left( \frac{\xi - 1}{\ln \xi} \right)^2 - 1 \right] \varepsilon_v \varepsilon A / L, \quad (1)$$

$$\Delta G = \left( \frac{\xi + 1}{2} + \frac{1 - \xi}{\ln \xi} \right) \kappa_\beta A / L, \quad (2)$$

where,  $\xi = \kappa_\alpha / \kappa_\beta$ ,  $\kappa_\alpha$  and  $\kappa_\beta$  are conductivity at both ends of the CPL, and  $L$  is thickness of the CPL.  $\varepsilon_v$ , permittivity of the vacuum, and  $A$ , area of cross-section of the CPL (equal to the area of the membrane or the electrode).

In order to clearly understand eqs. (1) and (2), a numerical simulation is performed, and the result is shown in Figure 7. As can be seen, with  $\varepsilon$ ,  $L$  and  $A$  fixed,



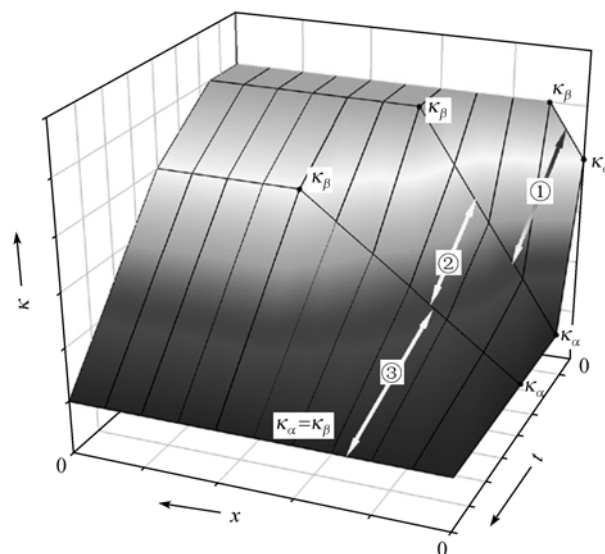
**Figure 7**  $\Delta CL$  ( $\varepsilon_v \varepsilon A$ ) (a) and  $\Delta GL/A$  (b) vs.  $\kappa_\alpha$  and  $\kappa_\beta$ , obtained by simulation. When  $\kappa_\alpha = \kappa_\beta$ , the results are meaningless (see eqs. (1) and (2)), and are substituted by 0.001 to facilitate plotting.

$\Delta C$  and  $\Delta G$  increase as the difference between  $\kappa_\alpha$  and  $\kappa_\beta$  increases. When  $\kappa_\alpha = \kappa_\beta$ , no relaxation show up (see the “holes” in the figures). In addition, if  $\kappa_\alpha$  and  $\kappa_\beta$  are fixed,  $\Delta C$  and  $\Delta G$  decrease as the thickness  $L$  increases.

### 2.3.3 Identification of concentration polarization mechanism and explanation to the relaxation phenomena.

To find out how changes in CPL affect the relaxation strength, we examine the changes in CPL in the adsorption and release processes respectively. Figure 8 shows the changes of CPL in the adsorption process. It is known that chitosan adsorbs SA from the solution due to its basic functional group  $-\text{NH}_2$ <sup>[4,5]</sup>. As adsorption proceeds, two CPLs are formed on both sides of the membrane. Wherein,  $\kappa_\alpha$ , the conductivity of the CPL at the boundary next to the membrane, is less than  $\kappa_\beta$ , the conductivity at the boundary next to bulk solution. When the adsorption amount is small, the difference between  $\kappa_\alpha$  and  $\kappa_\beta$  is not prominent; however, under such conditions, the thickness  $L$  of the CPL is very small, as a result, so the relaxation strength should be large, according to eqs. (1) and (2). This is consistent with what is observed in Figures 4(a), (b) and 5(a), (b).

With the membrane adsorbing SA from the solution near the membrane,  $\kappa_\alpha$  decreases and reaches the minimum (probably close to conductivity of distilled water<sup>[25]</sup>) in a short period of time. Meanwhile,  $\kappa_\beta$  decreases more slowly than its counterpart  $\kappa_\alpha$ , and thickness  $L$  of the CPL increases. This situation is exemplified in stage 1 shown in Figure 8, and at the end of stage 1, the difference between  $\kappa_\alpha$  and  $\kappa_\beta$  reaches the maxi-



**Figure 8** Diagram on CPL changes in the adsorption process.

imum. According to the simulation in section 2.3.2, the relaxation strength should also increase to the maximum. Indeed, the relaxation strength of the adsorption process of the thick membrane, showed in Figure 4(a), (b), is observed to increase to the maximum within 20 min, as predicted by the CPL mechanism. Contrary to the prediction, relaxation strength of the adsorption process at the thin membrane, shown in Figure 5(a), (b), does not increase in the very first period. This contradiction may be because that at the low concentration of SA,  $\kappa_\alpha$  decreases to the minimum ( $\Delta C$  and  $\Delta G$  increases to the maximum) so fast (perhaps even faster than the experimental operation) that the increasing stage of relaxation strength is not detected.

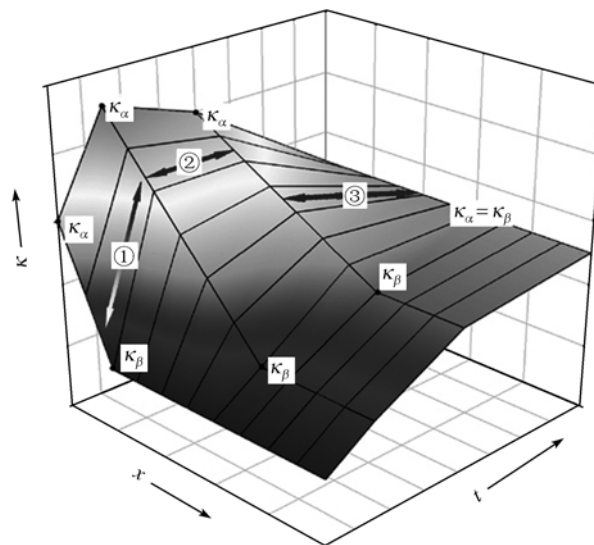
As the adsorption process goes on,  $\kappa_\beta$  continues to decline. At the same time,  $\kappa_\alpha$  is unchanged or increases slowly, so the difference between them becomes smaller. Meanwhile, the CPL thickness  $L$  increases. Eventually  $\kappa_\alpha$  equals to  $\kappa_\beta$  and the CPL disappears, implying that the adsorption stops. This situation is showcased by stages 2 and 3 in Figure 8. Accordingly, as the difference between  $\kappa_\alpha$  and  $\kappa_\beta$  becomes smaller and the CPL thickness  $L$  increases, the relaxation strength gradually declines, as observed in Figures 4(a), (b) and 5(a), (b).

It should be noted that at a certain moment in the adsorption process of the thick membrane (Figure 4 (a), (b)), higher initial concentration of SA leads to larger relaxation strength (especially  $\Delta G$ ). This may be due to that  $\kappa_\alpha$  (close to the conductivity of distilled water<sup>[25]</sup>) is much less sensitive to the initial concentration of SA than  $\kappa_\beta$ . Therefore increase in the SA initial concentration leads to larger difference between  $\kappa_\alpha$  and  $\kappa_\beta$ , and consequently bigger relaxation strength.

Differently, in the adsorption process by the thin membrane, at SA concentrations higher than  $0.1 \text{ mmol} \cdot \text{L}^{-1}$ , the relaxation strength decreases with SA concentration, until the relaxation is not discernable when SA concentration reaches  $0.2 \text{ mmol} \cdot \text{L}^{-1}$ . The slow adsorption by the very thin membrane may explain this. When the concentration of SA is relatively high, the slight decrease in acid concentration near the membrane due to the adsorption can be quickly supplemented, because the acid in the distance of the solution moves toward the membrane. Therefore,  $\kappa_\alpha$  decreases slightly and the difference between  $\kappa_\alpha$  and  $\kappa_\beta$  is not substantial enough to make the relaxation detectable.

Figure 9 shows the changes of CPL in release processes. The conductivity of CPL at the boundary adjacent to the membrane,  $\kappa_\alpha$ , is higher than  $\kappa_\beta$ , the conductivity at the other end of the CPL.  $\kappa_\alpha$  decreases after reaching the maximum, because the release rate initially is faster than the diffusion of SA into the bulk solution. On the other hand,  $\kappa_\beta$  gradually increases and then tends to plateau. The trends over time make the difference between  $\kappa_\alpha$  and  $\kappa_\beta$  increase first and then decreases. As a result, the relaxation strength increases, reaches maximum and then gradually decreases. This situation predicted by the CPL mechanism is confirmed by the experiment, as shown in Figures 4(c), (d) and 5(c), (d). In addition, Figures 4(c), (d) and 5(c), (d) also show that the use of

higher concentration of SA in adsorption process causes greater relaxation strength in corresponding release process. Conceivably, at higher SA concentration more SA is adsorbed by the chitosan membrane. Consequently, more SA will be released from the membrane in followed release process, and leads to CPLs with greater conductivity gradient.



**Figure 9** Diagram on CPL changes in the release process.

Based on the proposed CPL mechanism, the relaxation strength change in the adsorption or release is well explained. This also confirms that the formation of CPL is essential for the dielectric relaxations.

#### 2.4 CPL mechanism and diffusion dynamics

As discussed in section 2.3.2, if the conductivity gradient of CPL increases, the relaxation strength becomes more pronounced. Conductivity is determined by the concentration of conductive substances. If a complete numerical method for analyzing dielectric spectra of adsorption or release processes is established based on the CPL model, concentration gradient of the adsorbates in the solution can be obtained. Furthermore, dynamic changes of the concentration gradient can also be obtained as a result of continuous dielectric monitoring.

For the adsorption or release system, the concentration gradient of the adsorbates depends on two factors. One is the migration of the adsorbates in the solution; the other is the interaction between the membrane and the adsorbates. The former is reflected by the diffusion coefficient of substances, which can be easily obtained



from handbooks, so its impact may be deducted. Therefore, information on interactions between the membrane and the adsorbates can be obtained. Moreover, alternations of main mechanism of the adsorption or release processes in different stages can be studied. This information should be useful for designing absorbents used in controlled drug release or environment protection.

### 3 Conclusion remarks

In this study, DS is used to monitor the adsorption or release processes of SA at the chitosan membranes of two different thicknesses. The relaxation mechanism is confirmed to be caused by the concentration polarization layer (CPL) formed on both sides of the membrane. The identification of the mechanism provides a theoretical basis for establishing a quantitative method to obtain information of the membrane systems in the dynamic processes including adsorption and release. Based on the

theoretical model and corresponding analytical formula, and the characteristics of specific adsorption or release system, a theoretical analyzing method can be established. Electrical parameters (conductivity and permittivity) of the membrane and the solution, and structural parameters of the interface (such as thickness and concentration profile of the CPL) in the dynamic adsorption or release process of membrane can be obtained. Because the dielectric measurement on the entire system is a non-invasive computer-controlled process, this study provides a new way for applying DS in drug controlled release and environmental monitoring. In addition, dynamic concentration profile obtained from the dielectric analysis can be used to study the mechanism of the interactions between adsorbents and adsorbates. Further study on this adsorption and release processes, to calculate out the inner parameters through establishing calculation program, is in progress.

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