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Electrolytic conductivity behaviors and solution conformations of chitosan in different acid solutions

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Abstract

Electrolytic conductivity behavior of chitosan in strong acid solution (0.1 M hydrochloric acid) and in weak acid solution (0.1 M propionic acid, 0.1 M acetic acid and 0.1 M formic acid) and its effective factors such as temperature, salt, degree of deacetylation and molecule weight of chitosan were investigated. The inner structure of chitosan films formed from their above different acid solutions were observed with a scanning electron microscope (SEM). It was found that the electrolytic conductivity behaviors of chitosan in the above two-type acid solutions were absolutely different and were all concentration-dependent from which we can deduce that chitosan chains interact with carboxylic acid molecules strongly in weak acid solutions and entangle strongly with each other while chitosan chains have weak impact on counterions chlorions in hydrochloric acid solution and they become extended coils because of electrostatic repulsion. The structure of chitosan films observed from their SEM photos supports this conclusion firmly. Unchanging activation energy for conduction of chitosan in carboxylic acid solution after a certain concentration also demonstrates that there is order structure formed by chitosan and carboxylic acid molecules. This is the first paper supplying detailed electrolytic data about chitosan solution; therefore, it will stimulate further theoretical studies and promote the application of chitosan.

Keywords: Chitosan; Polyelectrolyte; Electrolytic conductivity; Solution conformation; Activation energy for conduction

1. Introduction

Chitin is the second most polysaccharide in nature next to cellulose and widely distributed as the component of the skeletal structure of crustaceans, insects, mushrooms and the cell wall of fungi. But its application is limited due to its lack of solubility in major solvents. Its partly deacetylated derivate, chitosan, which is a copolymer of β (1→4) linked 2-amino-2-deoxy-D-glucose and 2-acetamino-2-deoxy-D-glucose, is soluble in dilute acidic medium, so, it can be manufactured into chitosan films, gels, sponges, fibers and micro particles that are widely used in a large field such as food, cosmetics and pharmacy. Researchers in the above fields have found that the type of acid as solvent of chitosan has important influence on the property of chitosan product (Orienti, Cerchiara, Luppi, Bigucci, Zuccari and Zecchi, 2002; Ritthidej, Phaechamud, & Koizumi, 2002; Tengamnuay, Sahamethapat, Sailasuta, & Mitra, 2000). In our research on chitosan microspheres as carrier for drug, we also found that the type of acid such as strong acid hydrochloric acid and weak acid carboxylic acid has important effect on morphology and property of chitosan microspheres (Yang, Song, Li, & Fan, 2004). So, for rational use of chitosan and better understanding of the property of its product, it is essential to understand its solution behavior. There is a lot of studies on chitosan solution using rheology (Nyström, Kj&niksen, & Iversen, 1999; Desbrieres, 2002) and light scattering methods (Schatz, Pichot, Delair, Viton, & Domard, 2003a; Schatz, Viton, Delair, Pichot, & Domard, 2003b), but the solution conformation of chitosan and the influence of solvent on chitosan are still unclear and under debate (Pedroni, Schulz, Gschaider, & Andreucetti, 2003).

Electrolytic conductivity is a powerful tool in studying transport process in electrolytic solutions for its very high accuracy in measurements (Vink, 1981). When chitosan dissolves in acidic medium, it becomes a kind of polyelectrolyte carrying positive charges due to the presence of amino groups, which may be protonated. So, in this study, we applied the electrolytic conductivity method to study the conductivity behavior of chitosan in different acid solution in detail and

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found that the electrolytic conductivity behaviors of chitosan in different acid solutions were absolutely different. From this, we can deduce that the solution conformation of chitosan in different acid solution is different and this results into different charge conduction mechanism in different chitosan acid solution. The SEM photos of films formed by different chitosan acid solutions supports this conclusion firmly. Moreover, temperature, salt, degree of deacetylation (DD) and viscosity-average molecular weight (Mv) of chitosan have important influence on the specific conductivity of chitosan solution and experiments investigating these factors supply more proofs on our conclusion. This is the first paper supplying detailed electrolytic data about chitosan solution; therefore, it will stimulate further theoretical studies on this polyelectrolyte system.

2. Experimental

2.1. Measurement of electrolytic conductivity behaviors of chitosan in different acid solution

Four chitosan samples prepared in our laboratory were used in this study: chitosan 1 ($DD=96.3\%$, $Mv=6.92\times10^5$), chitosan 2 ($DD=94.4\%$, $Mv=9.30\times10^5$), chitosan 3 ($DD=82.3\%$, $Mv=4.87\times10^5$), and chitosan 4 ($DD=81.9\%$, $Mv=1.17\times10^6$). Degree of deacetylation (DD) of the above chitosan samples was determined by UV spectrophotometric method (Du, Lu, Yue, Wang, Di and Cui, 1994). Viscosity-average molecular weight (Mv) was determined from Mark–Houwink Eq. (Wang, Bo, Li, & Qin, 1991). Prior to use, all chitosan samples were purified as follows: dissolution in a 0.2 M acetic acid solution, filtration through millipore membranes of decreasing porosity (from 3 to 0.22 μm), precipitation with 1 M sodium hydroxide, rinsing until reaching the conductivity of distilled water and then lyophilization. Hydrochloric acid, formic acid, acetic acid, propionic acid and sodium chloride were analytic grade and purchased from Beijing Chemical Reagents Company (Beijing, China). The specific conductivity of distilled water used in this experiment was always in the range of 7.5×10^{-5} S/m to 8.7×10^{-5} S/m.

All measurements were carried out with a DDS-11A conductimeter (Shanghai, China) in a water thermostat (Shanghai, China) that was maintained within temperature range of ±0.05 K. Repeated runs were carried out at least three times. The reproducibility of the data was within $\pm0.5\%$.

2.2. Scanning electron microscope of chitosan films prepared from different chitosan acid solutions

Fifteen milligram/milliliter chitosan formic acid solution, chitosan acetic acid solution, chitosan propionic acid solution and 15 mg/mL chitosan hydrochloric acid solution were dropped on aluminum foils to form chitosan films. The surface morphology of the chitosan films were observed with a scanning electron microscope (SEM) (JEOL, Japan) after coated with gold films.

3. Results and discussion

3.1. Electrolytic conductivity behaviors and solution conformations of chitosan in strong acid solution and weak acid solution are different

Specific conductivity (κ) of chitosan 1 ($DD=96.3\%$, $Mv=6.92\times10^5$), dissolved in 0.1 M hydrochloric acid, decreases linearly with the increase of chitosan concentration from 10^{-4} to 15 mg/mL (Fig. 1(a)). But the electrolytic conductivity behavior of chitosan 1 in weak acid is different and the conductivity curves can be divided into four parts (Fig. 1(b1) and (b2)): (1) C ranging from 10^{-4} to 0.4 mg/mL for chitosan in 0.1 M propionic acid and chitosan in 0.1 M acetic acid, and C ranging from 10^{-4} to 1.5 mg/mL for chitosan in 0.1 M formic acid, κ decreases with the increase of chitosan concentration, (2) C ranging from 0.4 to 0.6 mg/mL (plateau concentration) for chitosan in 0.1 M propionic acid and chitosan in 0.1 M acetic acid, and C ranging from 1.5 to 2.0 mg/mL (plateau concentration) for chitosan in 0.1 M formic acid, κ is almost unchanged, (3) C ranging from 0.6 to 1.0 mg/mL for chitosan in 0.1 M propionic acid and chitosan in 0.1 M acetic acid, and C ranging from 2.0 to 3.0 mg/mL for chitosan in 0.1 M formic acid, κ increases slowly with the increase of chitosan concentration, and then (4) C ranging from 1.0 to 15.0 mg/mL for chitosan in 0.1 M propionic acid and chitosan in 0.1 M acetic acid, and C ranging from 3.0 to 15.0 mg/mL for chitosan in 0.1 M formic acid, κ increases linearly with the increase of chitosan concentration.

This phenomenon is very interesting and we think different solution conformation and conduction mechanism of chitosan in different acid solution lead to it. When chitosan dissolves in 0.1 M hydrochloric acid, it becomes a polycation because amino groups on chitosan chains bind free hydrions and chitosan chains become extended coils due to electrostatic repulsion. Chitosan carrying positive charges cannot move orderly and cannot transport charges, so there are only chlorions and unbound hydrions transport charge. With the increase of chitosan concentration, more hydrions are bound, the amount of free ions to transport charge decreases, so the conductivity of chitosan hydrochloric acid solution decreases with the increase of chitosan concentration. In Fig. 1(a), when chitosan concentration is 15.08 mg/mL, which stoichiometricly equals to about 0.09 M amino groups, the specific conductivity of the solution is 0.7 S/m, which is close to the specific conductivity 0.64 S/m of 0.1 M chlorions (Dobos, 1975). This means chitosan almost binds hydrions completely and there are only chlorions and few remaining hydrions transporting charge while protonated chitosan barely contributes to conduction. Moreover, there is electrostatic attraction between free chlorions and polycation, and this will influence the specific conductivity of chlorions.

But for chitosan in 0.1 M formic acid solution, 0.1 M acetic acid solution and in 0.1 M propionic acid solution, the conductivity behaviors of chitosan solution show that there is a transforming process of chitosan solution conformation and charge conduction mechanism in these solutions with the

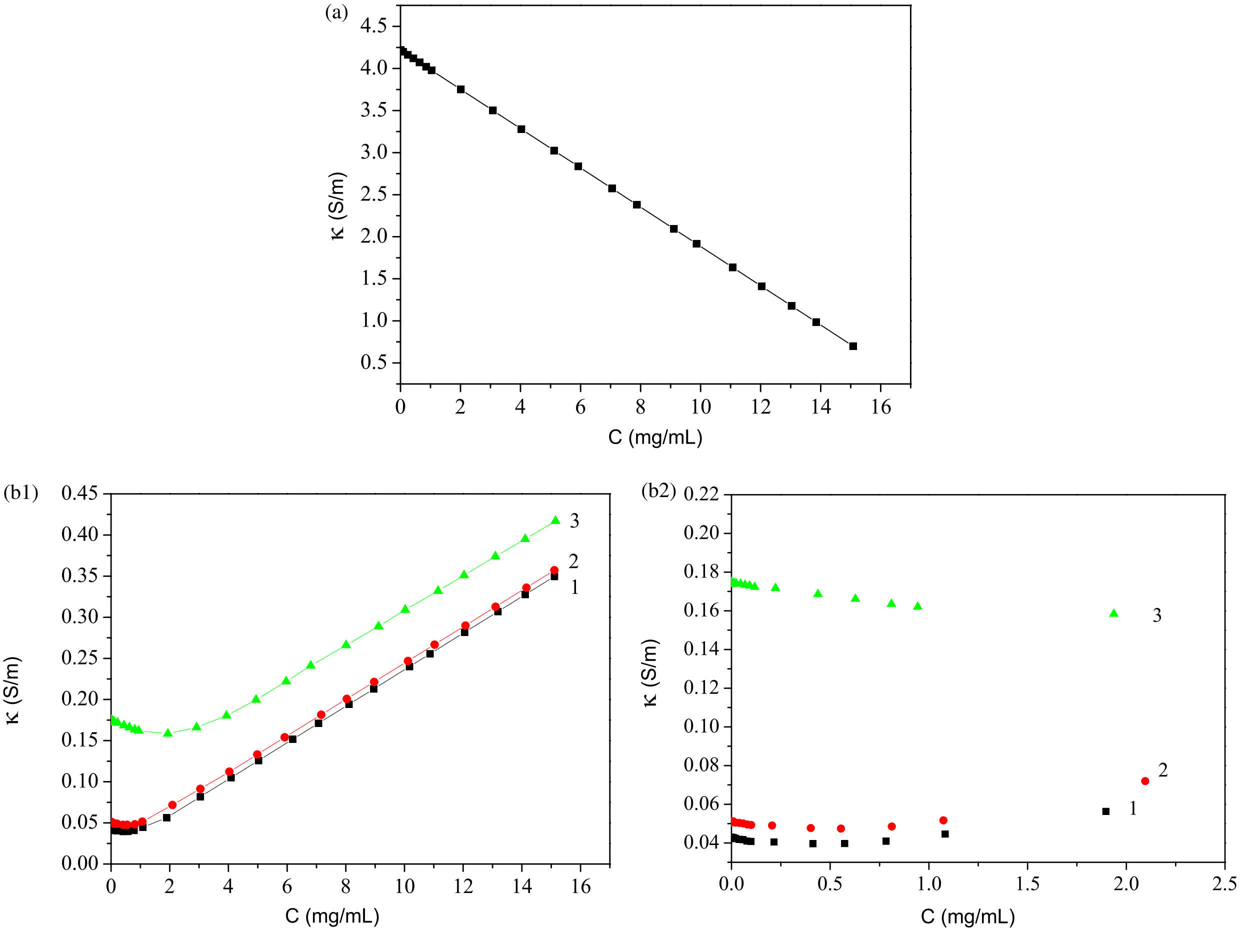

Fig. 1. The electrolytic conductivity behaviors of chitosan 1 in different acid solutions. (a) The electrolytic conductivity behavior of chitosan 1 dissolves in 0.1 M hydrochloric acid solution; (b1) the electrolytic conductivity behaviors of chitosan 1 dissolves in (1) 0.1 M propionic acid solution, (2) 0.1 M acetic acid solution, and (3) 0.1 M formic acid solution; (b2) enlarged plots of the electrolytic conductivity behaviors of chitosan 1 dissolves in (1) 0.1 M propionic acid solution, (2) 0.1 M acetic acid solution, and (3) 0.1 M formic acid solution.

increase of chitosan concentration. For 0.1 M formic acid solution, 0.1 M acetic acid solution and 0.1 M propionic acid solution, there are dissociated carboxylic acidic ions (R-COO$^-$), hydrions (H$^+$) and undissociated carboxylic acid molecules (R-COOH). In Fig. 1(b1) and (b2), when chitosan dissolves in these weak acid solutions, amino groups first binds dissociated hydrions and leads to the slight decrease of specific conductivity, at this time, it is free ions transport charge and chitosan chains carrying positive charges repel each other and become extended coils because of electrostatic action same as that in hydrochloric acid solution. And then when dissociated hydrions are bound completely, with the increase of chitosan

Table 1

Plateau concentrations of specific conductivity of chitosan 1 acid solutions at different temperature

Acid	T(K)	K	α	C_{H+} (mol/L)	Cp (mg/mL)
Propionic acid	298	1.33×10^{-5}	0.01147	0.001147	0.4125–0.5735
	308	1.305×10^{-5}	0.01136	0.001136	0.4125–0.5735
	318	1.255×10^{-5}	0.01114	0.001114	0.2153–0.4125
	328	1.195×10^{-5}	0.01087	0.001087	0.2153–0.4125
Acetic acid	298	1.75×10^{-5}	0.01314	0.001314	0.4012–0.5545
	308	1.73×10^{-5}	0.01306	0.001306	0.4012–0.5545
	318	1.67×10^{-5}	0.01284	0.001284	0.206–0.4013
	328	1.59×10^{-5}	0.01253	0.001253	0.206–0.4013
Formic acid	298	1.77×10^{-4}	0.0412	0.00412	1.525–1.936
	308	1.75×10^{-4}	0.041	0.0041	1.525–1.936
	318	1.68×10^{-4}	0.04016	0.004016	0.6278–0.8105
	328	1.61×10^{-4}	0.03933	0.003933	0.6278–0.8105

K is dissociation constant of acids; α is degree of electrolytic dissociation; C_{H+} is the concentration of dissociated hydrogen ions in 0.1 M carboxylic acid solution C_p is the plateau concentration of specific conductivity of chitosan 1 solution. The electrochemistry data of propionic acid, acetic acid and formic acid is from reference (Dobos, 1975)

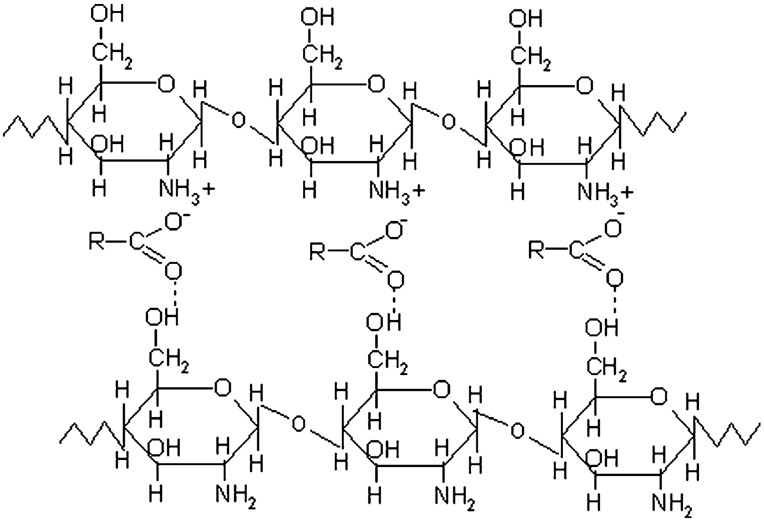

Fig. 2. Complex of chitosan and carboxylic acid molecules formed through partly ion cross-linking bond and hydrogen bond.

concentration, more chitosan begins to interact with undissociated carboxylic acid molecules by which charge are transported, so, the specific conductivity of chitosan solution begins to increase. As shown in Table 1, different carboxylic acid (propionic acid, acetic acid, formic acid) has different dissociation constant and the amount of dissociated hydrions in their 0.1 M solutions is different, so the plateau concentration that represents the transformation of conductivity of chitosan solution is different. At plateau concentration of conductivity, chitosan begins to interact with carboxylic acid molecules and form stable and order complex. Fig. 2 shows the complex formed by chitosan and carboxylic acid molecules through

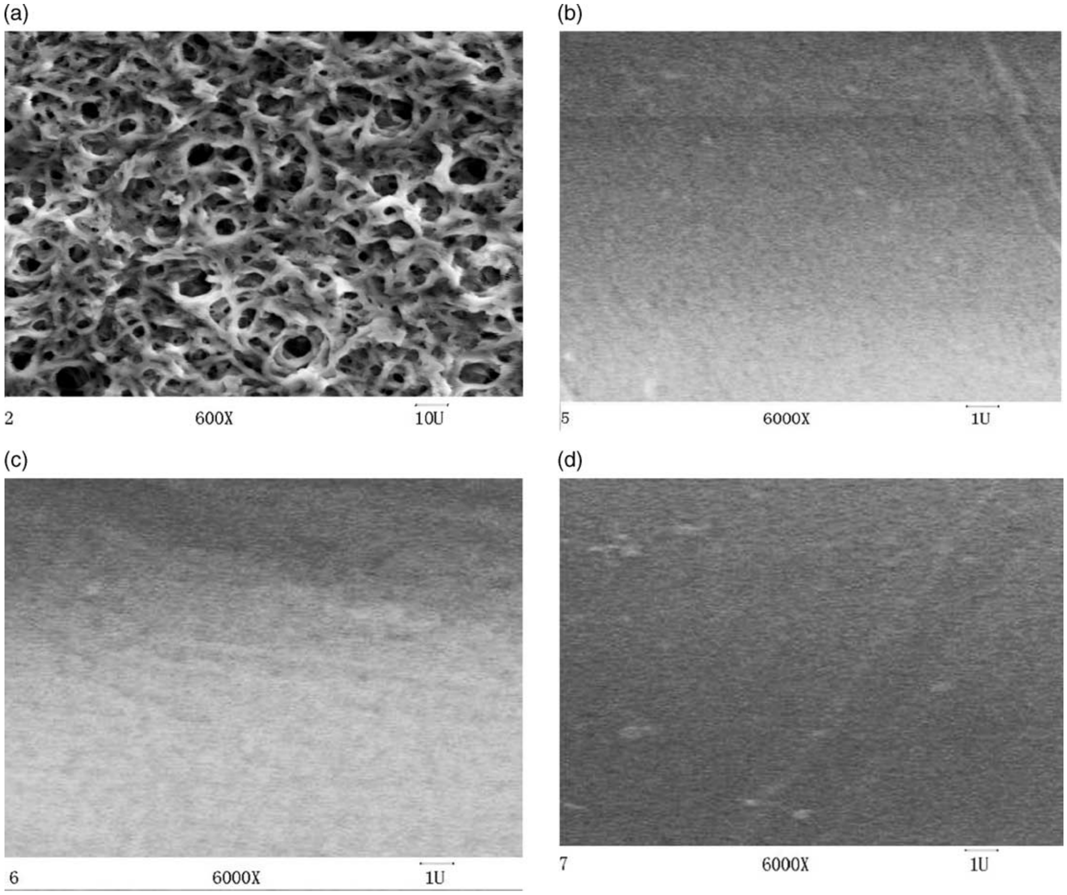

Fig. 3. SEM photos of chitosan film formed from 15 mg/mL chitosan acid solutions. (a) SEM photo of chitosan film formed from 15 mg/mL chitosan 1 hydrochloric acid aqueous solution; (b) SEM photo of chitosan film formed from 15 mg/mL chitosan 1 formic acid aqueous solution; (c) SEM photo of chitosan film formed from 15 mg/mL chitosan 1 acetic acid aqueous solution; (d) SEM photo of chitosan film formed from 15 mg/mL chitosan 1 propionic acid aqueous solution.

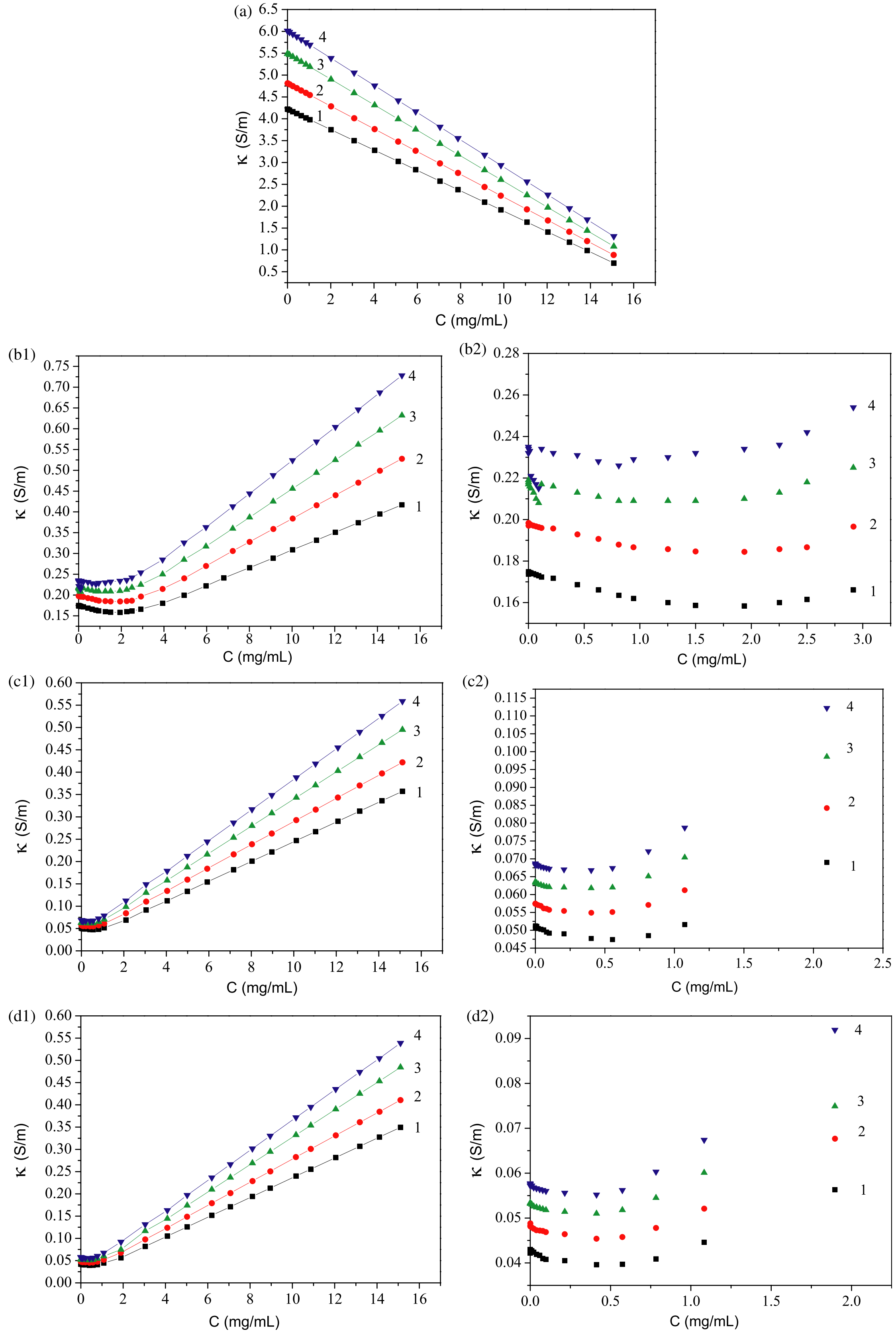

Fig. 4. Influence of temperature on the conductivity behavior of chitosan 1 in different acid solution. (1) 298 K; (2) 308 K; (3) 318 K; (4) 328 K. (a) chitosan 1 dissolves in 0.1 M hydrochloric acid solution; (b1) chitosan 1 dissolves in 0.1 M formic acid solution; (b2) enlarged plots of chitosan 1 dissolves in 0.1 M formic acid solution; (c1) chitosan 1 dissolves in 0.1 M acetic acid solution; (c2) enlarged plots of chitosan 1 dissolves in 0.1 M acetic acid solution; (d1) chitosan 1 dissolves in 0.1 M propionic acid solution; (d2) enlarged plots of chitosan 1 dissolves in 0.1 M propionic acid solution.

partly ion cross–linking bond of amino groups on chitosan chains with carboxylic acid and hydrogen bond of hydroxyl groups on chitosan chains with carboxylic acid. It is proposed that carboxylic acidic ions (R-COO$^-$) and H_3O^+ move orderly along this complex and transport charge. With the increase of chitosan concentration, more complex forms and the specific conductivity increases accordingly.

Besides, we think the plateau concentration 0.4–0.6 mg/mL of chitosan in 0.1 M acetic acid solution that represents the transformation of conductivity and conformation of chitosan is the aggregation concentration reported in other articles where the aggregation concentration is 1 mg/mL by the method of dynamic light scattering and pyrene fluorescene (Wu, Zhou, & Wang, 1995; Amiji, 1995). Therefore, the method of electrolytic conductivity is more sensitive than other methods and it can detect the aggregation of chitosan chains at the concentration of 0.4 mg/mL.

The film formed from a 15 mg/mL chitosan hydrochloric acid solution is hard and opaque and SEM photo (Fig. 3(a)) shows that the film has a lot of big pores the diameter of which is more than 10 μm. But the films formed from 15 mg/mL chitosan formic acid solution, chitosan acetic acid solution and chitosan propionic acid solution are all soft and transparent, and the SEM photos (Fig. 3(b–d)) show that the films are all dense. This sufficiently suggests that chitosan chains entangle strongly with each other in 0.1 M carboxylic acid solutions while those repel each other and become extended coils in 0.1 M hydrochloric acid solution. Different chitosan solution conformations lead to different phase behaviors of chitosan and produce different material properties.

3.2. Influence of temperature on the concentration-dependent conductivity behaviors of chitosan in different acid solutions

Fig. 4 shows the influence of temperature on the concentration-dependent conductivity behaviors of chitosan 1 in different acid solutions. In Fig. 4(a), the specific conductivity (κ) of chitosan in 0.1 M hydrochloric acid increases with the increase of temperature and the electrolytic conductivity behavior of chitosan still depends on the chitosan concentration. In Fig. 4(c1,c2,d1,d2), the specific conductivity of chitosan acetic acid solution and chitosan propionic acid solution increases with the increase of temperature and these two chitosan acid solutions are stable to heat even at 318 and 328 K. But in Fig. 4(b1) and (b2), the high dilute concentration region of chitosan formic acid solution is unstable to heat at 318 and 328 K. The specific conductivity of chitosan in dilute concentration region from 10^{-4} to 0.08 mg/mL decreases with

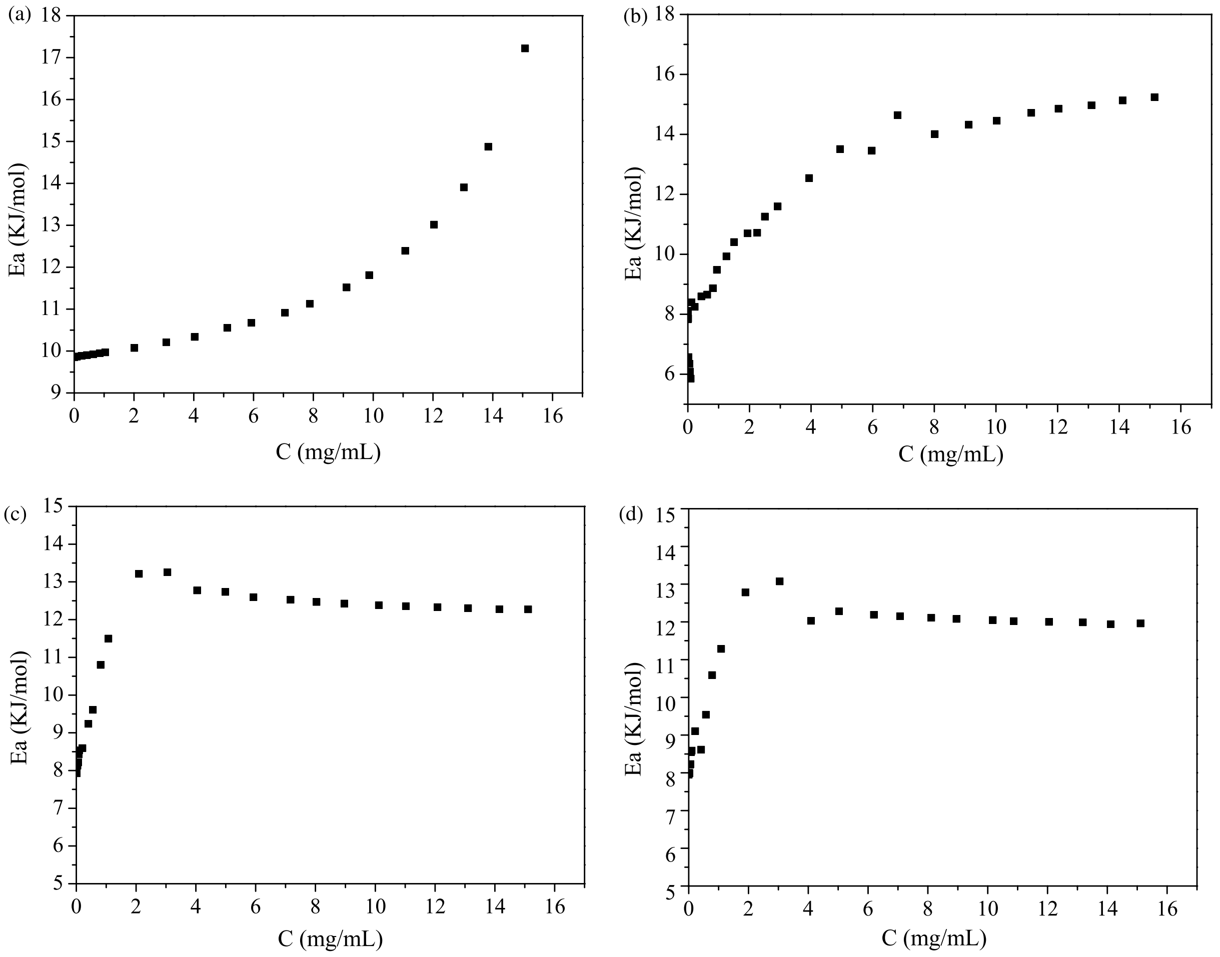

Fig. 5. Concentration-dependent activation energy for conduction of chitosan 1 in different acid solution. (a) chitosan dissolves in 0.1 M hydrochloric acid solution; (b) chitosan dissolves in 0.1 M formic acid solution; (c) chitosan dissolves in 0.1 M acetic acid solution; (d) chitosan dissolves in 0.1 M propionic acid solution.

the increase of concentration and at 0.1 mg/mL, it again increases and then its conductivity behavior is same as that at 298 and 308 K. In addition, for chitosan in weak acid solution, temperature has effect on the plateau concentration of the specific conductivity. As shown in Table 1, the dissociation constant of weak acid decreases with the increase of temperature; therefore, the amount of dissociated hydrions decreases and lower chitosan concentration is enough to bind these hydrions, so, the plateau concentration of specific conductivity decreases. The change of plateau concentration

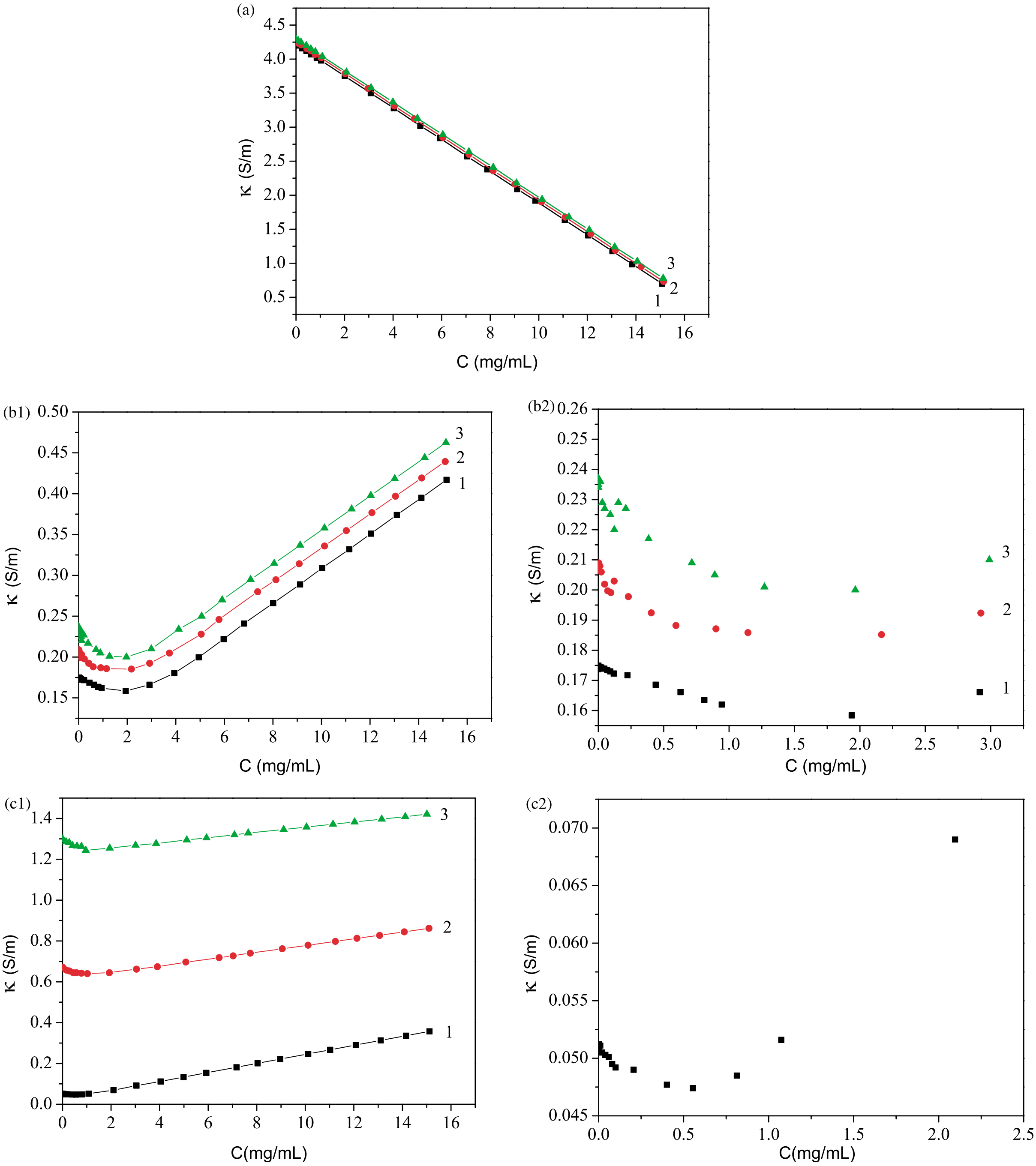

Fig. 6. Influence of sodium chloride on the conductivity behavior of chitosan 1. a (1) 0.1 M hydrochloric acid solution, (2) 0.1 M hydrochloric acid solution +0.0025 M sodium chloride, (3) 0.1 M hydrochloric acid solution +0.005 M sodium chloride; (b1) (1) 0.1 M formic acid solution, (2) 0.1 M formic acid solution +0.0025 M sodium chloride, (3) 0.1 M formic acid solution +0.005 M sodium chloride; (b2) enlarged plots of chitosan 1 in (1) 0.1 M formic acid solution, (2) 0.1 M formic acid solution +0.0025 M sodium chloride, (3) 0.1 M formic acid solution +0.005 M sodium chloride; (c1) (1) 0.1 M acetic acid solution, (2) 0.1 M acetic acid solution +0.05 M sodium chloride, (3) 0.1 M acetic acid solution +0.1 M sodium chloride; (c2) Enlarged plot of chitosan 1 in 0.1 M acetic acid solution; (c3) Enlarged plot of chitosan 1 in 0.1 M acetic acid solution +0.05 M sodium chloride; (c4) Enlarged plot of chitosan 1 in 0.1 M acetic acid solution +0.1 M sodium chloride. (d1) (1) 0.1 M propionic acid solution, (2) 0.1 M propionic acid solution +0.05 M sodium chloride, (3) 0.1 M propionic acid solution +0.1 M sodium chloride; (d2) Enlarged plot of chitosan 1 in 0.1 M propionic acid solution; (d3) Enlarged plot of chitosan 1 in 0.1 M propionic acid solution +0.05 M sodium chloride; (d4) Enlarged plot of chitosan 1 in 0.1 M propionic acid solution +0.1 M sodium chloride.

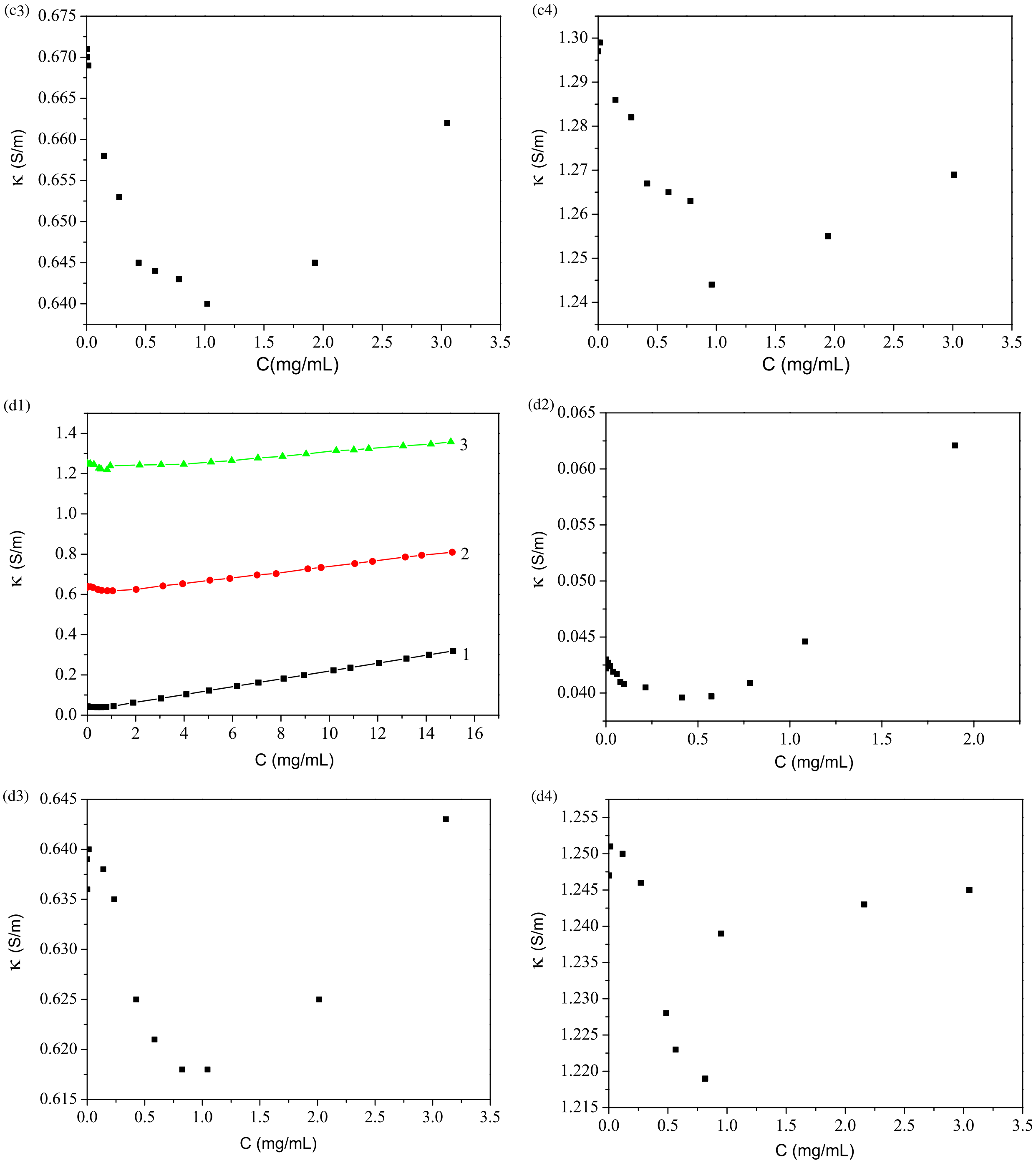

Fig. 6 (*continued*)

confirms firmly that there is transform of solution conformation and conduction mechanism of chitosan in weak acid solution with the increase of chitosan concentration.

In all cases, the Arrhenius plots of ln κ vs. $1/T$ of every chitosan concentration shows good linear relation in the temperature range of 298–328 K (listed in Supporting information) and the activation energy for conduction calculated accordingly is found to be dependent on chitosan concentration and this dependence is completely different for chitosan in strong acid solution and in weak acid solution (Fig. 5). For chitosan in 0.1 M hydrochloric acid, Ea increases with the increase of chitosan concentration (Fig. 5(a)) and fits into the correlation $\mathrm{Ea}=9.78+0.177\ \mathrm{e}^{(c/4.05)}$, $R^2=0.9958$ and finally achieves the maximum 17.2 KJ/mol at 15.08 mg/mL. This confirms that in chitosan hydrochloric acid solution, there is electrostatic attraction between chlorions with polycation, and with the increase of chitosan concentration, this electrostatic attraction increases and results in the exponential increase of Ea. But for chitosan in 0.1 M acetic acid and chitosan in 0.1 M propionic acid, Ea increases from beginning and achieves the maximum 13.26 KJ/mol

(Fig. 5(c)) and 13.07 KJ/mol (Fig. 5(d)), respectively at 3.04 mg/mL and then maintains almost constant 12.46 KJ/mol ((Fig. 5(c)) and 12.07 KJ/mol (Fig. 5(d)), respectively with the increase of chitosan concentration. For chitosan in 0.1 M formic acid (Fig. 5(b)), Ea increases from beginning and achieves the maximum 14.64 KJ/mol at 6.81 mg/mL and then increases slightly with the increase of chitosan concentration and achieves maximum 15.20 KJ/mol at 15.14 mg/ml. The unchanging Ea for conduction of chitosan in 0.1 M acetic acid solution and in 0.1 M propionic acid solution suggests strongly that chitosan interacts with carboxylic acid molecules and forms stable and order structure that is presented in Fig. 2. For chitosan in 0.1 M formic acid solution, this complex also forms but it is less stable than that in 0.1 M acetic acid solution and in 0.1 M propionic acid solution.

3.3. Influence of salt on the concentration-dependent conductivity behaviors of chitosan in different acid solutions

Different amount sodium chloride was added into acid solution to dissolve chitosan because different chitosan acid solution has different sensitivity to salt. Fig. 6 shows that under the condition that chitosan can dissolve completely, the specific conductivity of chitosan solution with added sodium chloride increases the amount of specific conductivity of corresponding added salt and the added salt can not change the concentration-dependent conductivity behavior of chitosan solution. In Fig. 6(a,b1,b2), κ of 0.0025 and 0.005 M sodium chloride are 0.0369, 0.0677 S/m, respectively and κ of chitosan in 0.1 M hydrochloric acid solution and in 0.1 M formic acid solution with 0.0025 and 0.005 M sodium chloride increases 0.0369, 0.0677 S/m, respectively. Similarly, in Fig. 6(c1–c4,d1–d4), the specific conductivity of chitosan in 0.1 M acetic acid solution and in 0.1 M propionic acid solution with 0.05 and 0.1 M sodium chloride increases 0.618 and 1.214 S/m that are the corresponding specific conductivity of added sodium chloride. In addition, from Table 2 we can see that the plateau concentration of the specific conductivity of chitosan in weak acid solution with added sodium chloride increases due to the screening effect produced by added sodium chloride. Moreover, this screening effect is so strong that the plateau concentration turns into a point when chitosan dissolves in 0.1 M acetic acid solution with 0.1 M sodium chloride and 0.1 M propionic acid solution with 0.1 M sodium chloride. In general, the complex of chitosan with carboxylic acid in weak acid solution formed at concentrated region is stable to added salt, especially for chitosan in acetic acid solution and in propionic acid solution.

3.4. Influence of DD and Mv of chitosan on the concentraton-dependent conductivity behaviors of chitosan in different acid solutions

Viscosity-average molecular weight (Mv) and degree of deacetylation (DD), which is defined as the molar ratio of N-amino-glucose units to N-amino-glucose units and N-acetamide-glucose units of chitosan, are two characteristic parameters of chitosan and have important effect on properties of chitosan. Here the electrolytic conductivity behaviors of chitosan 1 (DD=96.3%, Mv=6.92×10^5) and chitosan 2 (DD=94.4%, Mv=9.30×10^5) that has close DD but different Mv and chitosan 3 (DD=82.3%, Mv=4.87×10^5) and chitosan 4 (DD=81.9%, Mv=1.17×10^6) that also has close DD but different Mv were investigated and the effect of DD and Mv of chitosan on the electrolytic conductivity behaviors of chitosan in different acid solution were presented in Fig. 7. We can see from Fig. 7(a), for chitosan in 0.1 M hydrochloric acid solution, the specific conductivity of chitosan samples that have close DD is close such as chitosan 1 and chitosan 2, chitosan 3 and chitosan 4 but chitosan samples that have higher DD has lower specific conductivity. For chitosan sample that has close DD but different Mv, the higher the Mv is, the higher the specific conductivity is. chitosan binds hydrions in 0.1 M hydrochloric acid solution and chitosan that has higher DD has more N-amino-glucose units and can bind more hydrions thus leads to the lower specific conductivity. For those chitosan samples that has close DD but different Mv, under the same concentration unit mg/mL, chitosan with high Mv has lower molar concentration compared to chitosan with low Mv, in this case, there are less amine groups available to interact with protons for high Mv chitosan; therefore, the specific conductivity of chitosan with high Mv is high. But in Fig. 7(b1,b2,c1,c2,d1,d2), for chitosan in weak acid solution, the effect of DD and Mv of chitosan on specific conductivity is different from which in 0.1 M hydrochloric acid solution because the conduction mechanism of chitosan in these two-type solvent is different. In weak acid solution, chitosan that has higher DD and lower Mv has higher conductivity because chitosan with high DD can form more complex and chitosan with low Mv has more amine groups under the same concentration unit mg/mL compared with chitosan with high Mv, which also can form more complex and make more charges be transported. Moreover, Table 3 shows that DD has effect on the plateau concentration of chitosan. chitosan with lower DD has less N-amino-glucose units and in the same weak acid solution it needs more molecules to bind hydrions; therefore, its plateau concentration is higher than that of chitosan with high DD.

Table 2
The influence of the added sodium chloride on the plateau concentration of specific conductivity of chitosan 1 acid solutions

Solvent	Plateau concentration (mg/mL)
0.1 M propionic acid	0.4125–0.5735
0.1 M propionic acid + 0.05 M sodium chloride	0.825–1.045
0.1 M propionic acid + 0.1 M sodium chloride	–
0.1M acetic acid	0.4013–0.5545
0.1 M acetic acid + 0.05 M sodium chloride	0.58–0.78
0.1 M acetic acid + 0.1 M sodium chloride	–
0.1 M formic acid	1.0–1.9
0.1 M formic acid + 0.0025 M sodium chloride	1.14–2.165
0.1 M formic acid + 0.005 M sodium chloride	1.27–1.965

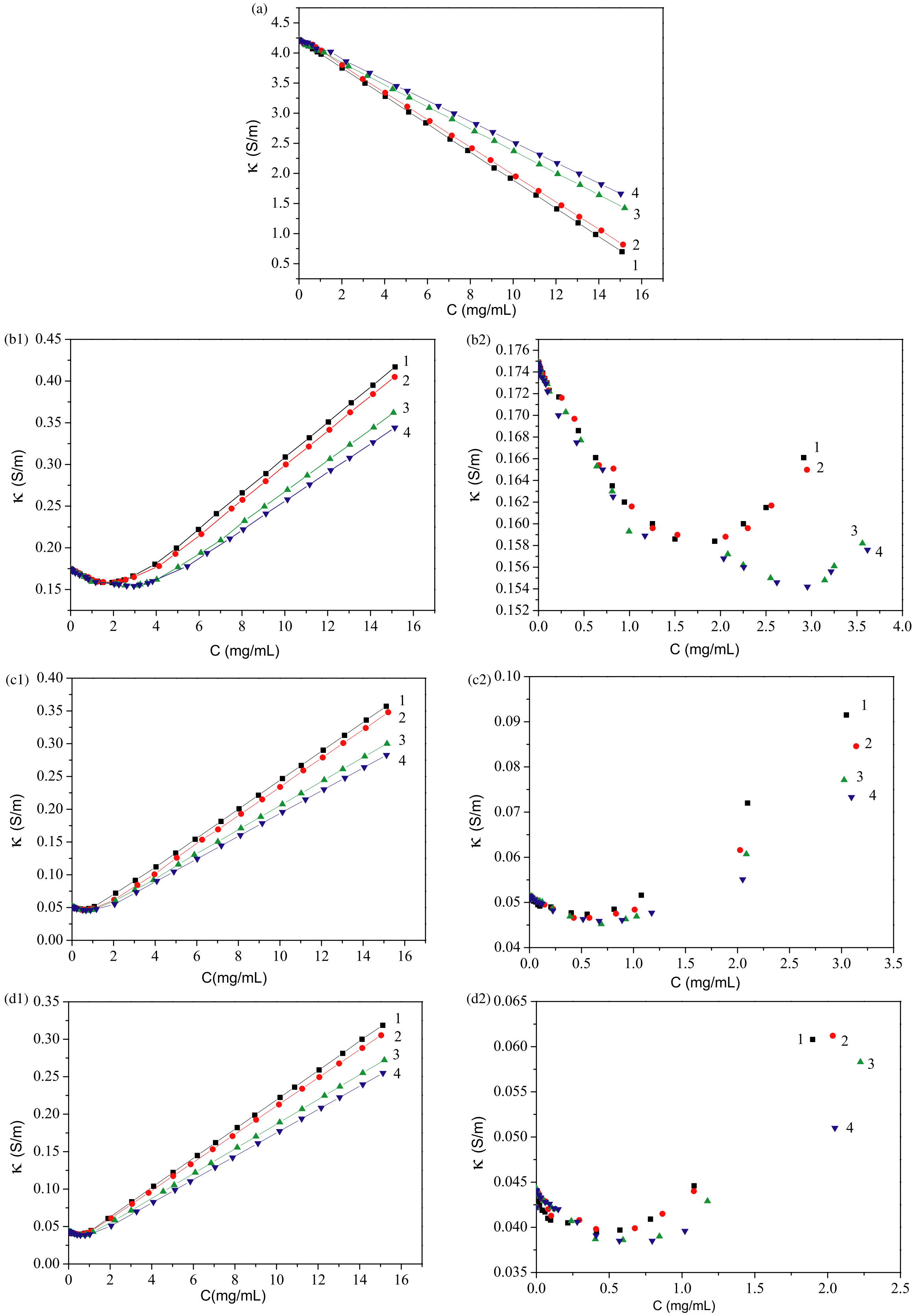

Fig. 7. Influence of DD and Mv on the conductivity behavior of chitosan in different acid solution. (1) chitosan 1 (DD = 96.3%, Mv = 6.92×10^5); (2) chitosan 2 (DD = 94.4%, Mv = 9.30×10^5); (3) chitosan 3 (DD = 82.3%, Mv = 4.87×10^5); (4) chitosan 4 (DD = 81.9%, Mv = 1.17×10^6). (a) chitosan samples dissolves in 0.1 M hydrochloric acid solution; (b1) chitosan samples dissolves in 0.1 M formic acid solution; (b2) enlarged plots of chitosan samples dissolves in 0.1 M formic acid solution; (c1) chitosan samples dissolves in 0.1 M acetic acid solution; (c2) enlarged plots of chitosan samples dissolves in 0.1 M acetic acid solution; (d1) chitosan samples dissolves in 0.1 M propionic acid solution; (d2) enlarged plots of chitosan samples dissolves in 0.1 M propionic acid solution.

Table 3
The plateau concentration of electrolytic conductivity of different chitosan in different acid solutions

Solvent	Plateau concentration (mg/mL)			
	Chitosan 1	Chitosan 2	Chitosan 3	Chitosan 4
0.1 M propionic acid	0.4125–0.5735	0.41–0.675	0.595–0.8	0.57–0.795
0.1 M acetic acid	0.422–0.5545	0.425–0.575	0.69–0.925	0.67–0.89
0.1 M formic acid	1.525–1.936	1.525–2.055	2.55–3.145	2.62–2.955

4. Conclusions

In this paper, we discussed the conductivity behaviors of chitosan in different acid solutions and found that the electrolytic conductivity behaviors of chitosan in weak acid solution and in strong acid solution were absolutely different from which we can deduce that in 0.1 M formic acid aqueous solution, 0.1 M acetic acid aqueous solution and in 0.1 M propionic acid aqueous solution, there is strong interaction between chitosan and carboxylic acid molecules and this action further leads to strong attraction between chitosan chains and makes them entangle with each other while in 0.1 M hydrochloric acid solution, chitosan has little interaction on counterions chlorions and chitosan chains repel each other and become extended coils because of electrostatic action. This different solution conformation determines the conductivity and phase behaviors of chitosan in different acid solutions. Besides, temperature, salt, DD and Mv of chitosan have important effect on chitosan concentration-dependent electrolytic conductivity behavior and experiments investigating these factors provide more proofs on our conclusion. Since no theory has been developed to describe these experimental findings completely, we believe the data of experiments would stimulate further theory development and application of chitosan.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2005.09.024

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