

Ion Sorption by Polyamide with Consideration of Ionic Interaction and Other Physical Interactions

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SYNOPSIS

A modified Donnan model is discussed with consideration of physical interactions in the ion sorption by polyamide as a function of the influence of ions in the system. Lyotropic numbers and the salt effect on water-structure changes are considered to describe their influence on the physical interactions between the sorbate and the sorbent. It is found that some electrolytes, such as sulfates and phosphates, can increase the sorption of some negatively charged ions (e.g., acid dyes) on positively charged polyamide if salt concentration is high (e.g., $> 0.5M$), after the initial decrease of ion sorption at a low salt concentration range. This result is difficult to explain by the model that treats all interactions other than ionic interaction as a constant. The modified Donnan model explains both the decrease and increase of ion sorption with increasing salt concentration quantitatively. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Although there are many different approaches for the modeling of ion sorption by solid polymers that have electrical charges in aqueous solutions,¹⁻¹⁶ one of the best approaches is the Donnan model. This model has been successfully applied to predict and explain ion sorptions by polyamides and polyacrylonitriles.^{7,12,13} Based on the Donnan model, McGregor and his co-workers developed a graphic method that simplified the implicit function of the model by using dimensionless groups.^{11,15,16} The basic equations for this model are as follows:

$$C_i^f = \lambda^{z_i} K_i C_i^s \quad (1)$$

$$\sum_i Z_i \lambda^{z_i} K_i C_i^s + \sum_k \frac{B_k}{1 + (K_{B_k} / \lambda K_{H^+} C_{H^+}^s)} - \sum_j \frac{A_j}{1 + (\lambda K_{H^+} C_{H^+}^s / K_{A_j})} = 0 \quad (2)$$

where i is the i th ionic species in the system; f , s ,

the polymer (fiber) phase and external solution phase, respectively; B_k , the concentration of the k th type of basic group in the polymer; A_j , the concentration of the j th type of acidic group in the polymer; H^+ , the hydrogen ion; Z_i , the electrical charge on the i th ion with sign; λ , the Donnan distribution coefficient; C_p^q , the concentration of the p th ion in the q th phase; K_i , the ionic distribution coefficient of the i th ion; and K_{A_j} , K_{B_j} , the dissociation coefficients of A_j and B_j , respectively.

Equation (1) is derived from thermodynamics.¹⁷ Equation (2) is based on the assumption of electrical neutrality in the polymer phase.⁷ In this approach, λ is related to the equilibrium electrical potential difference between the polymer phase and the solution. λ can be solved by eq. (2). It is a function of ionic interaction between polymer and ions.¹⁸ K_i includes all the other interactions in the ion sorption. It was treated as a constant that was independent in the presence of other ions. Therefore, C_i^f can be obtained from eq. (1) by substituting the value of λ .

The major disadvantage of this approach is that those interactions included in K_i are generally affected by other ions. For example, it is believed that hydrophobic interaction plays an important part in ion sorption by polyamides.¹⁹ It is also well known

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that hydrophobic interaction is greatly influenced by electrolytes through their effects on water structure.¹⁸ In other words, K_i is a function of not only the i th ion, but also other ions. Some of these ions are kosmotropes (water-structure maker); others are chaotropes (water-structure breaker).²⁰ According to Refs. 20 and 21, we can have the following series:



The anions preceding chloride are kosmotropes. The anions following chloride are chaotropes. The chloride anion is considered to be neutral to the water structure. Kosmotropes decrease the entropy of the system so as to increase the free energy of the solution phase. Chaotropes decrease the free energy of the solution by increasing the entropy. Therefore, K_i increases with addition of kosmotropes but decreases by adding chaotropes. Lyotropic numbers²¹ can be used to describe the electrolyte effects on hydrophobic interaction quantitatively. A detailed discussion of salt effects on hydrophobic interaction was given in Ref. 18.

The term hydrophobic interaction was originally used to describe the tendency of hydrophobic groups, such as alkyl chains, to associate together and escape from an aqueous environment.¹⁹ But current studies found that this interaction was actually the summation of a long-range interaction (Lifshitz-van der Waals interaction) and a short-range interaction (mainly hydrogen bonds), not a real hydrophobic interaction.²² In this paper, we call all these interactions "physical interactions." According to this definition, there are basically three different interactions in the ion-polymer sorption: ionic interaction, physical interactions, and chemical interactions. Chemical interactions are those with the formation of chemical bonds such as covalent bonds between the sorbent and the sorbate. They do not exist in our system.

The disadvantages of treating K_i as a constant were observed by Alberghina and his colleagues during their study of salt effects on cationic dye sorption by polyacrylonitriles.¹³ If K_i is a constant, and since the addition of any electrolytes will decrease the ionic interaction between the negatively charged polymer and positively charged dye ion, the ionic attraction of the dye ion by the polymer will always decrease.¹³ But, as a matter of fact, they observed the increase of dye equilibrium sorption with increasing concentrations of some salts. This phenomenon was explained by a modified Donnan model with the consideration of K_i as a function of the effects of other ions in the system.²³

In this paper, we study the effects of electrolytes on sorption of dye ions by polyamide. In addition to the effect of electrolytes on ionic interaction, electrolytes also affect the physical interactions. With the consideration of the effects of all ions on the sorption of an ion, a modified Donnan model was developed.²³ This model treats K_i as a function of other ions in terms of their activities, lyotropic numbers, and other properties. An empirical equation of K_i was developed²³ and used in this study [eq. (3)]:

$$K_i = K_{i0} + \sum_x k_x \left(\frac{T}{N} \right)_x^m a_x^n \quad (3)$$

where x is the x th electrolyte; a , the activity of an electrolyte. The molar concentration is used as an approximation; K_{i0} , the ionic distribution coefficient when there are no other electrolytes in the system; k , m , constants depending on the sorption condition and the properties of electrolytes; $n = 1.25$, a constant independent of other variables; and T , N , lyotropic numbers of cations and anions given in Ref. 21.

In eq. (3), the changes of physical interactions, other than ionic interaction, with the properties and concentrations of other electrolytes in the system are considered. Equations (1)–(3) give a more widely covered model than does the Donnan model currently used.

The objective of this article was to use this modified Donnan model for the discussion of ion sorption by polyamide, especially in those systems with high concentrations of electrolytes such as sulfates and phosphates. Sulfates and phosphates are strong kosmotropes.²¹ Their existence greatly increases the physical interactions between ion and polymer. The modified Donnan model considers this change of physical interactions by eq. (3). It is therefore more suitable than the model that treats K_i as a constant.

EXPERIMENTAL

Materials

Dyes used for this study were C.I. Acid Blue 40 and Acid Green 20. Acid Blue 40 is a monosulfonate dye, whereas Acid Green 20 is a bisulfonate dye. We chose dyes with different charge numbers in solution to study the feasibility of the model. Commercial dyes were used directly in this work. The percentage of dye in the commercial product was obtained by weighing the extract in N,N -dimethylformamide (DMF) and was used to calculate dye sorption. The

sorbent was a nylon 6,6 woven fabric #361 from Testfabrics, Middlesex, NJ. Salts used in this work were NaCl from Fisher Scientific, Fair Lawn, NJ; NaNO₃, NaH₂PO₄, and Na₂SO₄, from E. M. Science, Gibbstown, NJ; CH₃COONa·3H₂O from Fisher Scientific; and CH₃COOH, from Mallinckrodt, Paris, KY, were used to adjust the pH of the solution. All the chemicals were air-dried for 2 h at 105°C before weighing.

Ion Sorption

Ion sorption was performed in a sealed Erlenmeyer flask that was immersed in a shaking water bath at a temperature of 90°C for 2 h. For the sorption, 0.250 g of the fabric were used with a liquor-to-goods ratio of 160 : 1; 4.6 mM acetic acid and 1.0 mM of sodium acetate were used to adjust the pH to 4.0. After sorption, the pH of the solution was the same. The dye concentration was determined by light absorbance measurements at λ_{\max} with a model U-2000 spectrophotometer from Hitachi of Tokyo, Japan. Dye sorption was calculated from the difference in dye concentration before and after dyeing. Because it was difficult to adjust the equilibrium dye concentration (C_D^s) to exactly 10 mmol/L by using a finite dyebath, experimental data points in the figures for the study of salt effects with $C_D^s = 10$ mmol/L were from the regression curves of the sorption isotherms. The correlation coefficients of the regression curves were all larger than .995. Experimental data points in other places were all the original data.

Calculated Dye-sorption Curves

All the sorption results from the experiment were presented in this article by data points, whereas the calculated results from the modified Donnan model were given by curves with the consideration of physical interactions between polymer and ions as functions of other ions in the system. The calculation was based on eqs. (1)–(3). A subroutine, NEQNF, of the International Mathematical and Statistical Library²⁴ was used for the solution of the equations. This subroutine solves a system of nonlinear equations by using the Levenberg–Marquardt algorithm and a finite-difference approximation to Jacobian.

Constants in the Modified Donnan Model

Ionic Distribution Coefficient K_i

K_i is a function of physical interactions between i th ion and the polymer. The magnitude of K_i changes

with the properties and activities of other ions in the solution [eq. (3)]. We assume that the change of K_i for simple electrolytes, such as Na₂SO₄, NaH₂PO₄, NaCl, and NaNO₃, with the addition of other ions is negligible. This is because of their small ionic size. The increase of entropy due to their sorption has no obvious difference with or without the presence of other electrolytes. In this work, we treat the K_i of simple electrolytes as constants. Table I lists K_i values for all the ions of simple electrolytes used in this work for both Acid Blue 40– and Acid Green 20–polyamide systems. The data in Table I are the best fit data to the modified Donnan model. The differences of K_i values between two dyeing systems show the dependence of distribution of simple electrolyte on dye properties as discussed in Ref. 23. The physical interactions between the ions in Table I and the polymer are affected by dyes. From Table I, K_{H^+} is much larger than all the other K_i 's. This is because of the very strong physical interactions between amino end groups of polyamide and the hydrogen ion.

K_D , the ionic distribution coefficient of dye, is a function of other ions in the solution. Equation (3), which was established for the modeling of ion sorption by polyacrylonitriles,²³ is also a good approach for ion sorption by polyamide. Constants of eq. (3) for this study are listed in Table II. K_{D_0} is the dye distribution constant when the system does not have any other electrolytes. k and m are constants depending on the properties of electrolytes. k also relies on the sorbent properties. But according to this study, both of them are independent of the dye properties. n is a constant that has the same value in both ion sorption by polyamide and polyacrylonitrile.²³ It is possible that n could be treated as a constant of the equation for all sorption systems.

T and N are lyotropic numbers given by Voet²¹ for cations and anions, respectively. T and N values of the ions used in this study are 100, 11.6, 10.0, 8.2,

Table I Ionic Distribution Coefficient (K_i) of Simple Electrolytes

Ion	K_i	
	Acid Blue 40	Acid Green 20
Na ⁺	0.028	0.007
H ⁺	5.00	5.00
SO ₄ ²⁻	0.006	0.005
HO ⁻	0.002	0.002
H ₂ PO ₄ ⁻	0.0005	0.001
Cl ⁻	0.030	0.015
NO ₃ ⁻	0.130	0.070

Table II Constants of Eq. (3)

		Acid Blue 40	Acid Green 20
K_{D_0}		400	70
n			1.25
k	Kosmotrope	5	
	Cl^-	0	
	Chaotrope	-5	
m	Kosmotrope	1	
	Cl^-	0	
	Chaotrope	-1	

and 2.0 for Na^+ , NO_3^- , Cl^- , H_2PO_4^- and SO_4^{2-} , respectively. The larger the T value or the smaller the N value, the stronger the effect of the ion on increasing physical attractions.

Ionization of Polyamide

Concentrations of basic (B) and acid (A) end groups of the polyamide are 3.6×10^{-2} equiv/kg and 9.0×10^{-2} equiv/kg, respectively, based on Peters' data for nylon 6,6.²⁵ The dissociation coefficients for basic end group (k_B) and acid end group (k_A) are 10^{-10} and 10^{-5} , respectively.⁷

RESULTS AND DISCUSSION

Figures 1 and 2 show the effects of different salts and their concentrations on equilibrium sorption of Acid Blue 40 and Acid Green 20. In these studies, we examine the effect of salts on dye sorption while the equilibrium dye concentrations in the solution are kept the same. The salt effects on dye sorption can be easily observed by this treatment. The differences among these salts are their anions. All of them have the same cation (Na^+) for the simplicity of the discussion. The experimental results in these figures show that for some salts such as chlorides and nitrates the dye sorption decreases by increasing salt concentration. This result can be explained by the ionic interaction between the salt and the polymer. The salt ions in the solution neutralize the charges on both the polymer and the dye. Therefore, the dye-fiber ionic interaction decreases and the equilibrium dye sorption decreases.

The function of decreasing ionic interaction is similar to any electrolytes. But for some electrolytes, such as sulfates and phosphates, although dye sorption decreases with increasing salt concentration at a low concentration range, the dye sorption is sub-

sequently increased by increasing the concentration of the electrolytes. The effect of the electrolytes on ionic interaction can only be used to explain the decrease of dye sorption at low electrolyte concentrations.

With consideration of both ionic interaction and physical interactions in the ion sorption and the knowledge of the effects of different ions on the physical interactions (in the literature, they are usually called hydrophobic interactions), these experimental results could be explained. As discussed, different ions of electrolytes have different effects on physical interactions between sorbate (e.g., dye ion) and sorbent (e.g., polyamide) because of their different effects on water structure. Kosmotropes decrease the entropy of water. This results in the increase of chemical potential of the solution phase and promotes the dye sorption. At the same time, like other electrolytes, kosmotropes decrease the ionic interaction between dye and polyamide. The change of dye sorption with salt concentration is the combined effects of the salt on both ionic and physical interactions. When salt concentration is low (e.g., $< 0.05M$), its effect on ionic interaction is stronger than that on physical interactions. As a combined result, the dye sorption decreases with increasing salt concentrations. With the increase of salt concentration, its effect on physical interactions increases. Once the change of chemical potential due to the increase of physical interactions (attraction) is larger than that due to the decrease of ionic interaction (attraction), the dye sorption increases with increasing salt concentrations.

The quantitative analysis of dye sorption in the presence of electrolytes can be performed by the modified Donnan model given in eqs. (1)–(3). The curves of Figures 1 and 2 were the calculated dye sorption. They show the satisfaction of the modified Donnan model to different salts in a broad range of salt concentration.

For sulfates and phosphates, since ionic attraction between dye and polyamide decreases but physical attractions increase with increasing the salt concentrations, and the rate of decreasing ionic attraction is higher than the rate of increasing physical attraction when the salt concentration is low, but is lower when the salt concentration is high, the concave shape of dye sorption with increasing salt concentration is expected. Since sulfate is a stronger kosmotrope than is dihydrogen phosphate, its effect on increasing physical attraction is stronger. When salt concentration is low, dye sorption in the bath with dihydrogen phosphate is similar to (Fig. 1) or even more than (Fig. 2) that with sulfate. This is

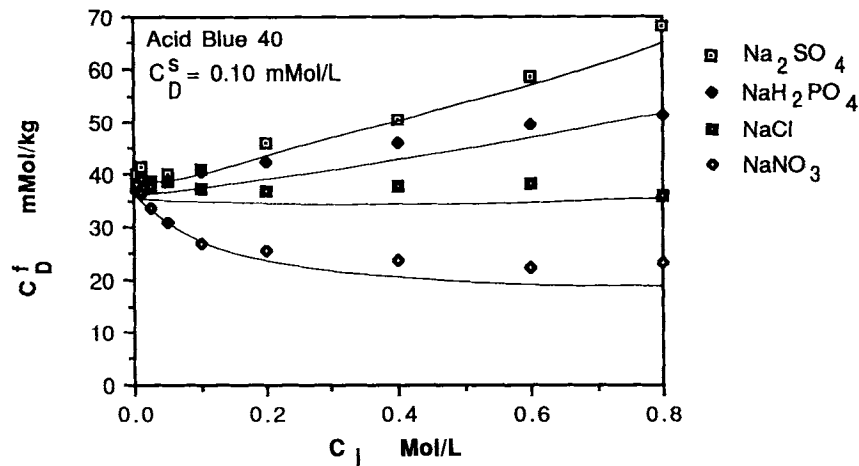


Figure 1 Effect of salt concentration and property on Acid Blue 40 sorption and comparison of calculated dye sorptions (curves) with experimental results (points).

because sulfate has two negative charges. With the same molar concentration, its effect on decreasing ionic attraction is stronger than that of dihydrogen phosphate. When salt concentration increases, its effect on physical interactions increases. Since sulfate has a stronger effect on increasing physical attraction than does dihydrogen phosphate, the increase of dye sorption with increasing sulfate concentration becomes faster than that with increasing dihydrogen phosphate concentration. In the figures, we see that the dye sorption increases more with sulfate than with dihydrogen phosphate when salt concentration is high.

Without the consideration of the change of physical interactions by electrolyte in the solution, this

concave sorption cannot be explained. Equation (3) includes the effect of electrolytes on ion sorption; therefore, the model gives a good prediction of the experimental results.

For chloride, since it is neutral to the influence on physical interactions, its effect on dye sorption is basically through its influence on ionic attraction between the sorbate and the sorbent. This is the reason that chloride decreases the dye sorption more than does phosphate and sulfate.

Since nitrate is a chaotrope, its addition decreases both ionic and physical attractions between sorbate and sorbent. The summation of these two effects causes the most decrease of dye sorption of all the salts studied (Figs. 1 and 2).

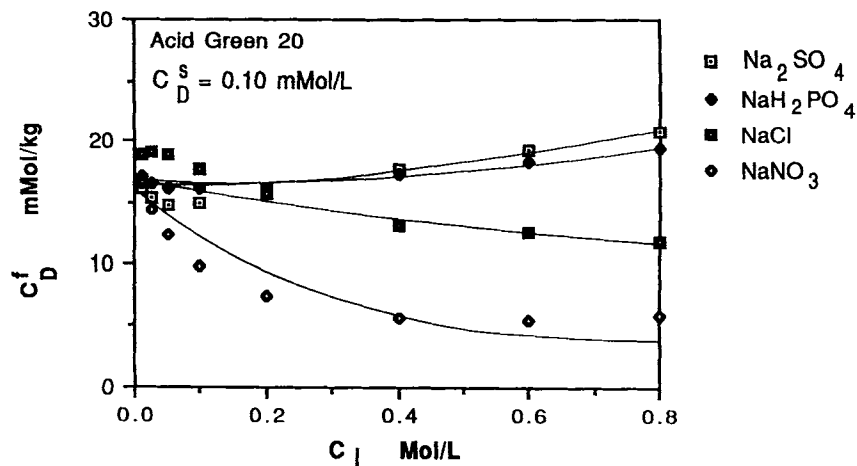


Figure 2 Effect of salt concentration and property on Acid Green 20 sorption and comparison of calculated dye sorptions (curves) with experimental results (points).

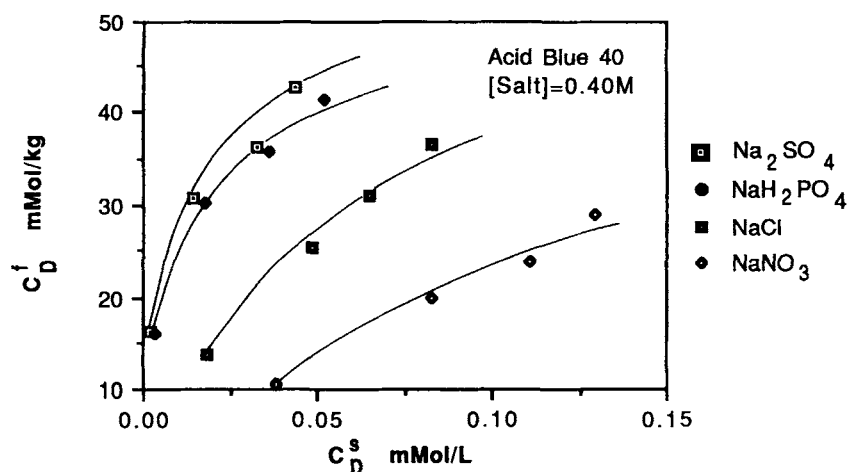


Figure 3 Effect of different salt properties on sorption isotherms of Acid Blue 40 on nylon 6,6 and comparison of calculated isotherms (curves) with experimental results (points).

To further test the feasibility of the modified Donnan model to different equilibrium dyebath concentrations, dye-sorption isotherms were calculated from eqs. (1)–(3) by changing the independent variable from salt concentration to equilibrium dye concentration in the bath. Figures 3 and 4 show examples of calculated isotherms (curves) with the comparison of experimental results (data points). In these experiments, the salt concentration keeps constant while the dye concentration changes. The model fits experimental results in a broad range of dye concentrations.

CONCLUSIONS

In addition to ionic interaction, physical interactions are also very important in the ion sorption by polyamide. The physical interactions change with the property and concentration of other ions in the solution. A modified Donnan model, which considers both ionic interaction and physical interactions and treats both interactions as functions of other ions in the system, is developed and used to explain the sorption of two anionic acid dye ions on polyamide in the presence of other ions. Some electrolytes, such

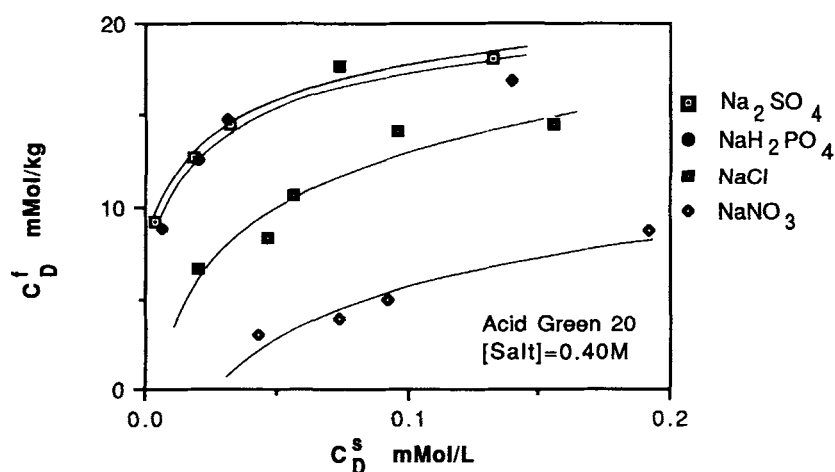


Figure 4 Effect of different salt properties on sorption isotherms of Acid Green 20 on nylon 6,6 and comparison of calculated isotherms (curves) with experimental results (points).

as sulfates and phosphates, can increase the sorption of negatively charged dye ions on positively charged polyamide because of their ability to increase the physical attraction between the dye and the polymer. Only at low concentration do all electrolytes decrease the sorption of negatively charged dye on polyamide. This is because that at low electrolyte concentration the effect of electrolyte on decreasing the ionic attraction between the dye and the polymer is stronger than that on increasing the physical attractions.

Using this modified Donnan model, the theoretical calculation satisfies the experimental data for both mono- and disulfonate acid dyes in a broad range of dye concentrations and salt concentrations whether the salt is a kosmotrope or a chaotrope.

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