

Adsorption/Ion-Exchange Behavior Between a Water-Insoluble Cationic Starch and 2-Chlorophenol in Aqueous Solutions

WU-CHUNG CHAN, TZU-PING FU

Civil Engineering Department, Chung-Hua Polytechnic Institute, Hsinchu, Taiwan 30067, Republic of China

Received 27 November 1997; accepted 10 June 1997

ABSTRACT: An investigation was undertaken regarding the removal of 2-chlorophenol from solutions using highly crosslinked cationic starch containing a tertiary amine group. The mechanism of removed 2-chlorophenol is affected by the pH of the aqueous phase. The nonionized and ionized species are removed by the adsorption and ion-exchange process, respectively. It has been found that the adsorption process predominated over the initial pH ranging from 2 to 6, the ion-exchange process predominated at initial pH 12, and both processes coexist over the initial pH ranging from 8 to 10. A method is suggested to determine the contribution of the nonionized and ionized species to remove 2-chlorophenol over the test pH range. The adsorption process is initially pH-independent, and the ion-exchange process is initially pH-dependent. The adsorption and ion-exchange processes are concentration-dependent, endothermic, and follow the Langmuir isothermal adsorption. The ΔH is 2.504 kcal/mol for the adsorption process and 3.580 kcal/mol for the ion-exchange process. The ion-exchange capacity is larger than the adsorption capacity. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1085–1092, 1998

Key words: water-insoluble cationic starch; 2-chlorophenol; adsorption; ion-exchange; tertiary amine

INTRODUCTION

The removal of toxic heavy metal ions and organic compounds from sewage and industrial wastewater has received much attention in recent years. However, the conventional precipitation process does not always provide a satisfactory removal rate to meet the pollution control limits; synthetic ion-exchange resins are often quite expensive as well. Many low-cost agricultural byproducts can bind heavy metal ions by adsorption, chelation, or ion-exchange. The use of agricultural byproducts (such as peanut

skins,^{1,2} onion skins,³ wool,^{4–7} and cotton⁸ for the adsorption of toxic heavy metal ions) has been previously reported. Also, it has been reported that the activated charcoal or the bentonite modified with tetraalkylammonium can be used to adsorb organic compounds.⁹

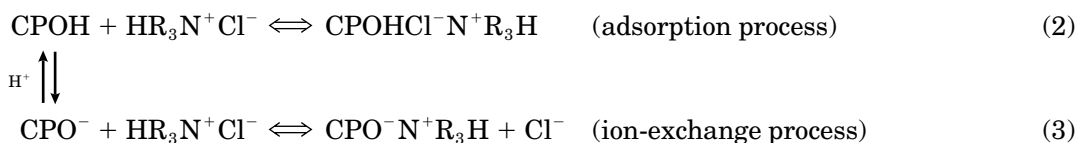
Starch is a naturally low-cost polymer that can be highly crosslinked with epichlorohydrin or other agents to make it water-insoluble. Chemical modification of the crosslinked starch with various reactive monomers yields ionomer products that can be used to remove heavy metal ions from wastewater. Xanthation of a crosslinked starch yields insoluble starch xanthate that has been shown to remove effectively heavy metal cations from wastewater.^{10,11} Insoluble starch products containing tertiary amine or quaternary ammo-

Correspondence to: W.-C. Chan.

Journal of Applied Polymer Science, Vol. 67, 1085–1092 (1998)
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exchange process entails exchanging the ionized species with the Cl⁻ of the cationic starch. There-

fore, the adsorption and ion-exchange processes can be proposed as the following scheme:



where HR₃N⁺Cl⁻ is the water-insoluble cationic starch. Equations (2) and (3) reveal that the adsorption process predominates in an acidic solution, and the ion-exchange process predominates in a basic solution.

To investigate the mechanisms of the adsorption and ion-exchange processes, we define a parameter ε that is the ratio of the equilibrium concentration of CPOH and of CPO⁻ at the desired initial pH and initial concentration (ε = [CPO⁻]/[CPOH]). The ε values for various initial pH values at the initial concentration range and 20°C are calculated by eq. (1) and K_{a,20°C}. The calculated ε values of initial pH 2, 4, 6, 8, 10, and 12 are ~ 2.82 × 10⁻⁷, 2.82 × 10⁻⁵, 2.82 × 10⁻³, 2.82 × 10⁻¹, 2.82 × 10¹, and 2.82 × 10³, respectively, over the initial concentration of 2-chlorophenol, ranging from 15 to 75 ppm. The ε values are < 10⁻² over the initial pH 2–6. The ε value is larger than 10² at the initial pH 12. For the sorption of pentachlorophenol onto natural solids collected by US EPA (Environmental Protection Agency) from the aqueous phase, it has been shown that > 90% of the sorption resulted from the sorption of ionized pentachlorophenol as the initial pH of solution is > 7.¹⁸ Thus, when the ε value is < 10⁻² (ε < 10⁻²), the mechanism of removed 2-chlorophenol from solution is regarded as the adsorption process that predominates. When the ε value is > 10² (ε > 10²), the mechanism of removed 2-chlorophenol from solution is regarded as the ion-exchange process that predominates. Therefore, we assume that the adsorption process predominates over the initial pH 2–6. The ion-exchange process predominates at the initial pH 12. Both the adsorption and ion-exchange processes coexist over the initial pH 8–10.

Effect of Initial pH

From our previous work, the degree of substitution of tertiaryamine was calculated as 0.73, and the theoretical adsorption capacity of the cationic starch was 2.80 mEq/g.¹³ The percentage of 2-

chlorophenol removed by the cationic starch for initial pH values of solution ranging from 2 to 12 at various initial concentration (15–75 ppm) and 30°C is shown in Figure 1. The percentage of removed 2-chlorophenol almost keeps constant over the initial pH range from 2 to 6. It then increases with increasing initial pH for each initial concentration. It is found that the initial pH range of the constant percentage of removed 2-chlorophenol corresponds to that of the predominated adsorption process. Thus, the percentage of 2-chlorophenol removed by the adsorption process is initially pH-independent.

Now, the average value of the percentages of removed 2-chlorophenol over the initial pH ranging from 2 to 6 is calculated as the percentage of 2-chlorophenol removed by the adsorption process. The percentage of removed 2-chlorophenol at the initial pH 12 is used as the percentage of 2-chlorophenol removed by the ion-exchange process. Be-

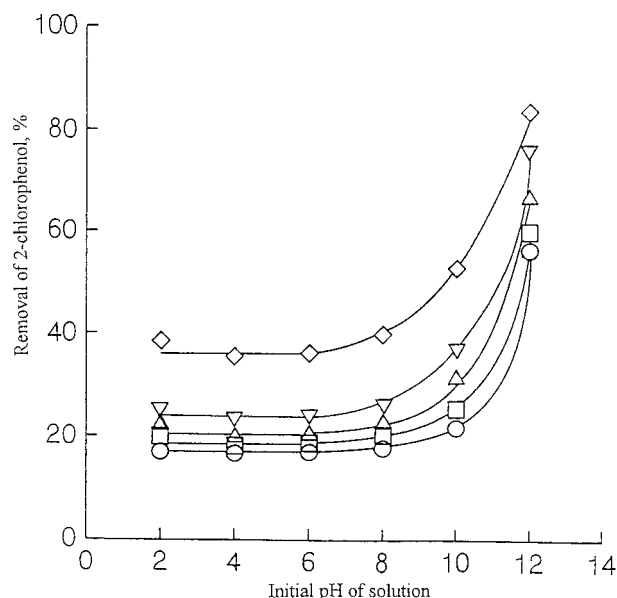


Figure 1 Effect of initial pH value of solution on the removal of 2-chlorophenol at various initial concentrations and 30°C: (◇) 15 ppm, (▽) 30 ppm, (△) 45 ppm, (□) 60 ppm, and (○) 75 ppm.

Table I Percentages of 2-Chlorophenol Removed by the Adsorption and Ion-Exchange Processes at 30°C: Adsorption Process

Initial pH	Initial Concentration of 2-Chlorophenol (ppm)				
	75	60	45	30	15
2	17.01%	19.95%	22.44%	25.47%	38.67%
4	16.87%	18.25%	19.91%	23.77%	35.73%
6	17.03%	18.78%	20.42%	24.20%	36.40%
8	16.97%	18.99%	20.92%	24.48%	36.93%
10	16.97%	18.99%	20.92%	24.48%	36.93%
12	—	—	—	—	—

The initial pH 12 is the predominant ion-exchange process, and the percentage for initial pH 8 and pH 10 takes the average values of the percentages of initial pH 2–6.

cause the percentage of 2-chlorophenol removed by the adsorption process is initially pH-independent, the calculated percentage of 2-chlorophenol removed by the adsorption process can be used as that in the initial pH range of the adsorption and ion-exchange processes coexisting. Then, the percentage of 2-chlorophenol removed by the ion-exchange process in the initial pH range of the adsorption and ion-exchange processes coexisting is calculated using the following equations:

$$[\text{CPOH}] + [\text{CPO}^-] = [\text{CPOH}]_i \cdot (\text{removed percentage}) \quad (4)$$

$$[\text{CPOH}] = [\text{CPOH}]_0 \cdot (\text{removed percentage by adsorption process}) \quad (5)$$

$$[\text{CPO}^-] = [\text{CPO}^-]_0 \cdot (\text{removed percentage by ion-exchange process}) \quad (6)$$

where $[\text{CPOH}]_i$ is the initial concentration of 2-chlorophenol, $[\text{CPOH}]_0$ is the concentration of CPOH species at the dissociation equilibrium before adsorption, and $[\text{CPO}^-]_0$ is the concentration

of CPO^- species at the dissociation equilibrium before ion-exchange. Thus, the percentage of 2-chlorophenol removed by the ion-exchange process can be calculated in the initial pH range where the adsorption and ion-exchange processes coexist.

The percentages of 2-chlorophenol removed by the adsorption and ion-exchange processes at various initial pH and concentration levels are listed in Tables I and II. The percentage of 2-chlorophenol removed by the ion-exchange process over the test initial concentration range (15–75 ppm) increases ~ 1.63 – 2.64 times as the initial pH value increases from 8 to 12. The result indicates that the percentage of 2-chlorophenol removed by the ion-exchange process is pH-dependent. Moreover, the percentage of 2-chlorophenol removed by the ion-exchange process is ~ 2.28 – 3.34 times that by the adsorption process. The result indicates that the ion-exchange capacity is larger than the adsorption capacity.

Effect of Concentration

The percentage of 2-chlorophenol removed by the cationic starch for the initial concentration of 2-

Table II Percentages of 2-Chlorophenol Removed by the Adsorption and Ion-Exchange Processes at 30°C: Ion-Exchange Process

Initial pH	Initial Concentration of 2-Chlorophenol (ppm)				
	75	60	45	30	15
2–6	—	—	—	—	—
8	21.43%	25.38%	29.41%	34.87%	51.50%
10	22.26%	25.91%	31.99%	38.11%	53.79%
12	56.68%	60.39%	67.20%	76.88%	84.13%

The initial pH 2–6 is the predominant adsorption process.

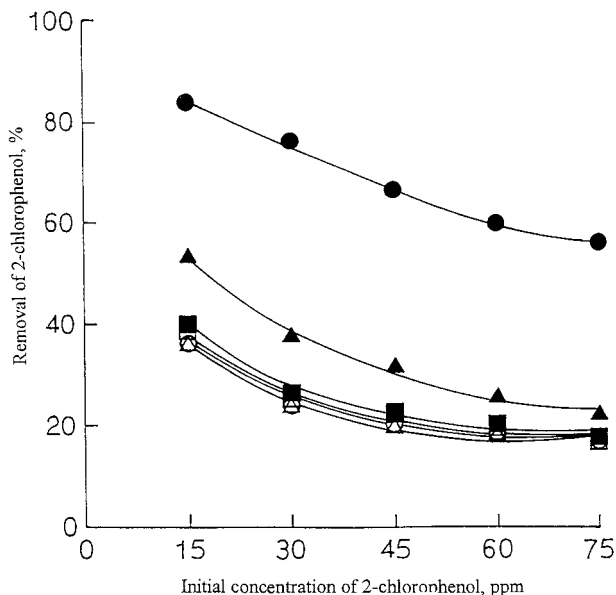


Figure 2 Effect of initial concentration on the removal of 2-chlorophenol at various initial pH's and 30°C: (□) pH 2, (△) pH 4, (○) pH 6, (■) pH 8, (▲) pH 10, and (●) pH 12.

chlorophenol ranging from 15 to 75 ppm at various initial pH's (2–12) and 30°C is shown in Figure 2. The percentage of removed 2-chlorophenol over the test initial pH range increased ~ 1.48–2.41 times, with decreasing initial concentration of 2-chlorophenol from 75 to 15 ppm. The result indicates that the removal of 2-chlorophenol is concentration-dependent. The percentage of 2-chlorophenol removed by the adsorption process increased from 16.97 to 36.93% (~ 2.18 times),

as the initial concentration decreased from 75 to 15 ppm. The percentage of 2-chlorophenol removed by the ion-exchange process increased from 56.68 to 84.13% (~ 1.48 times), as the initial concentration decreased from 75 to 15 ppm. The results indicate that removal of 2-chlorophenol by the adsorption process is more highly concentration-dependent than that by the ion-exchange process.

Adsorption Isotherm

The adsorption and ion-exchange isotherm for the removal of 2-chlorophenol by the cationic starch can be analyzed by the Langmuir adsorption isotherm expressed as:

$$\frac{C}{q_e} = \frac{1}{Qb} + \frac{C}{Q} \tag{7}$$

where C is the equilibrium concentration of 2-chlorophenol in solution (mg/L), q_e is the milligram of removed 2-chlorophenol per gram of cationic starch (mg/g), Q is the maximum amount of removed 2-chlorophenol per gram of cationic starch (mg/g), and b is the Langmuir constant (L/mg). Thus, a plot of C/q_e versus C should yield a straight line having a slope of $1/Q$ and an intercept of $1/Qb$ from which the values of Q and b can be readily attained.

The Langmuir plot of the data of 2-chlorophenol removed by the cationic starch at various initial pH's 2–12 and 30°C are shown in Figure 3 (only initial pH's 4 and 10 are shown). The relationship

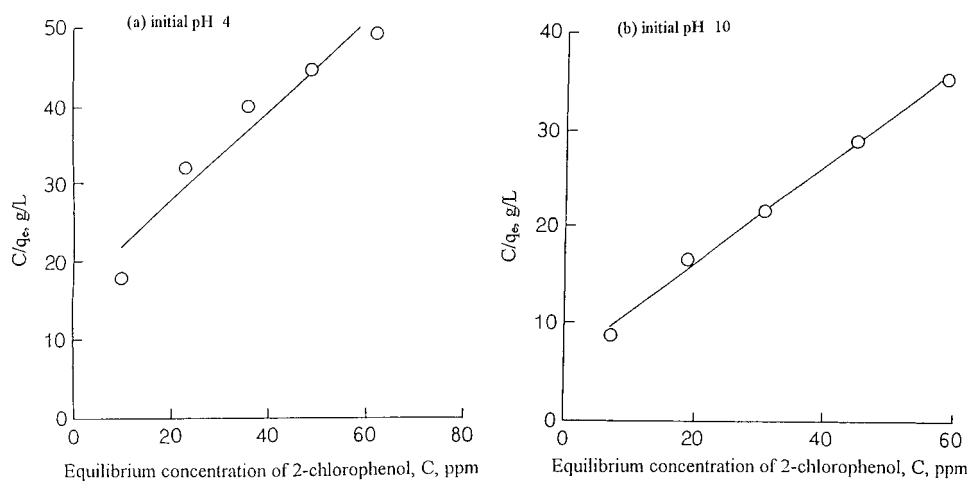


Figure 3 Langmuir plots of the removal of 2-chlorophenol at initial pH 4 and pH 10, and 30°C: (a) initial pH 4 and (b) initial pH 10.

Table III Langmuir Constant at Various Initial pH's

Langmuir Constant	Initial pH					
	2	4	6	8	10	12
Q (mg/g)	1.72	1.75	1.77	1.79	1.97	5.17
b (L/mg)	0.0443	0.0352	0.0362	0.0444	0.0836	0.1147

between C/q_e and C is linear, indicating that both the adsorption and ion-exchange behaviors follow the Langmuir adsorption isotherm. The Q and b values are listed in Table III. The Q values of initial pH's 2, 4, and 6 are 1.72, 1.75, and 1.77 mg/g, respectively, which is nearly constant. The Q values of initial pH's 8, 10, and 12 are 1.79 mg/g, 1.97 mg/g, and 5.17 mg/g, respectively, which increase with increasing initial pH. The results indicate that the adsorption capacity is initial pH-independent and the ion-exchange capacity is initial pH-dependent; and the ion-exchange capacity is larger than the adsorption capacity, as previously discussed.

Effect of Temperature

To investigate the temperature effect between the adsorption and ion-exchange processes, we select the initial pH's 4 and 10 as the test conditions for a series of various temperatures in the later experiments. The Langmuir plots of the data of 2-chlorophenol removed by the cationic starch for initial pH 4 and pH 10 at 40, 50, and 60°C are shown in Figures 4–6. It is found that both the adsorption (initial pH 4) and ion-exchange (initial pH 10) behav-

iors also follow the Langmuir adsorption isotherm at 40, 50, and 60°C. The change of apparent enthalpy (ΔH), free energy (ΔG), and entropy (ΔS) were calculated using the relationship:

$$\ln b = \ln b_0 - \Delta H/RT \quad (8)$$

$$\ln b = -\Delta G/RT \quad (9)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (10)$$

The values of ΔH , ΔG , and ΔS at each temperature are also listed in Table IV.

The Q values of the initial pH 4 increased from 1.75 to 2.02 mg/g, and those of the initial pH 10 increased from 1.83 to 2.11 mg/g, as the temperature increased from 30 to 60°C. Results indicate that both the adsorption capacity and ion-exchange capacity increase with temperature. The ΔH values of the initial pH 4 and pH 10 are 2.504 and 3.580 kcal/mol, respectively. The result demonstrates that both the adsorption and ion-exchange processes are endothermic. The ΔH value of the adsorption process is smaller than that of the ion-exchange process. The reason for such a

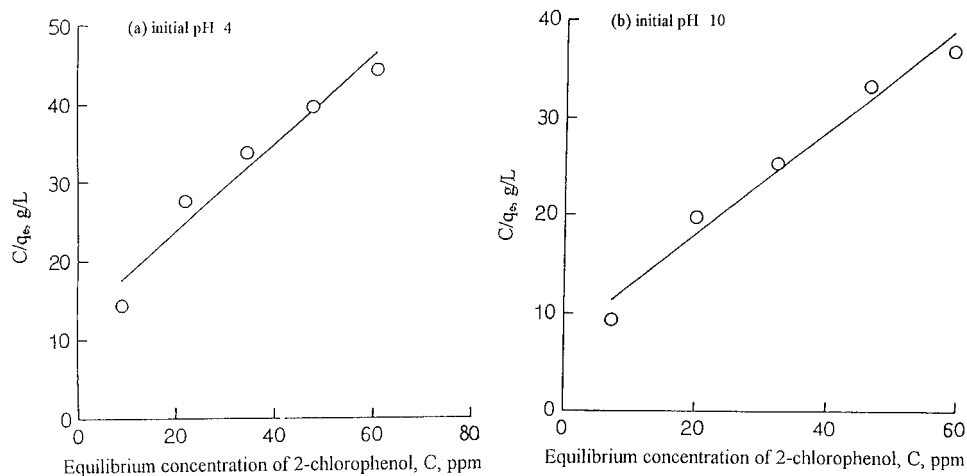


Figure 4 Langmuir plots of the removal of 2-chlorophenol at initial pH 4 and pH 10, and 40°C: (a) initial pH 4 and (b) initial pH 10.

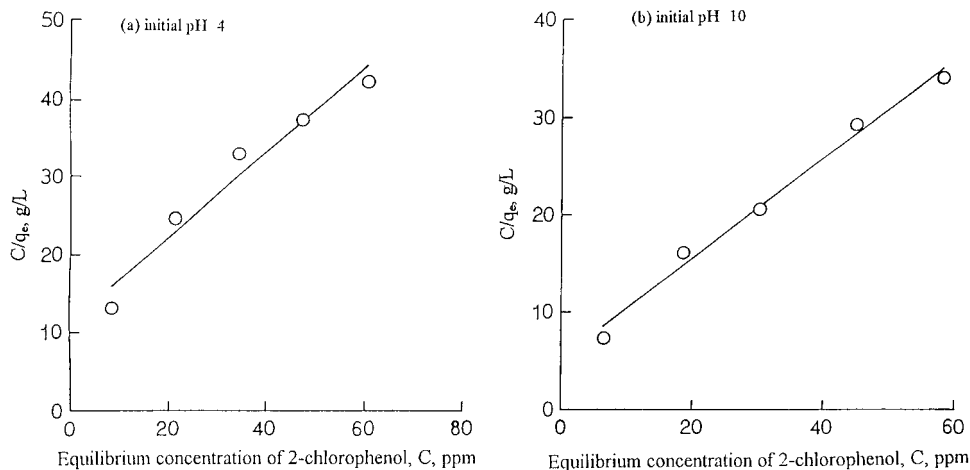


Figure 5 Langmuir plots of the removal of 2-chlorophenol at initial pH 4 and pH 10, and 50°C: (a) initial pH 4 and (b) initial pH 10.

discrepancy is that the covalent bond formed between the ionic species and cationic starch in the ion-exchange process is stronger than the hydrogen bond formed between the nonionic species and cationic starch in the adsorption process.

CONCLUSIONS

A highly crosslinked cationic starch containing a tertiary amine group can be used to remove 2-chlorophenol from aqueous solutions. The mechanism of removing 2-chlorophenol depends on the initial pH of solution. The nonionized and ionized species are removed by the adsorption and ion-exchange process, respectively. It has been found

that the adsorption process predominates over the initial pH, ranging from 2 to 6; the ion-exchange process predominates at initial pH 12; and both processes coexist over the initial pH, ranging from 8 to 10. A method is suggested to determine the contribution of the nonionized and ionized species to removal of 2-chlorophenol over the test pH range (pH 2–12). The adsorption process is initially pH-independent, and the ion-exchange process is initially pH-dependent. The adsorption and ion-exchange processes are concentration-dependent, endothermic, and follow the Langmuir isothermal adsorption. The ΔH is 2.504 kcal/mol for the adsorption process and 3.580 kcal/mol for the ion-exchange process. The capacity of the ion-exchange process is larger than that of the adsorption process.

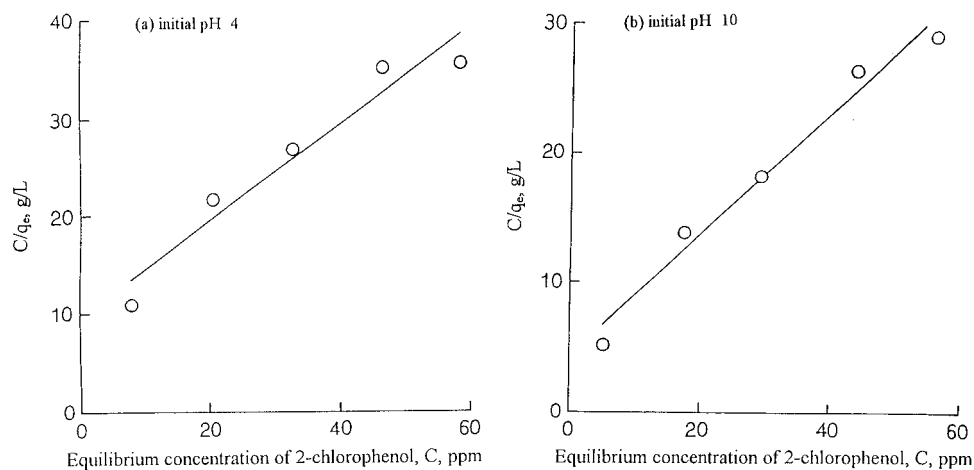


Figure 6 Langmuir plots of the removal of 2-chlorophenol at initial pH 4 and pH 10, and 60°C: (a) initial pH 4 and (b) initial pH 10.

Table IV Q , b , ΔH , ΔG , and ΔS Values of Initial pH 4 and pH 10 at Various Temperatures

Initial pH	Temperature (°C)	Q (mg/g)	b (L/mg)	ΔG (kcal/mol)	ΔS (kcal/mol)
4	30	1.75	0.0351	2.017	1.61
	40	1.81	0.0436	1.948	1.78
	50	1.84	0.0480	1.949	1.72
	60	2.02	0.0514	1.964	1.62
10	30	1.83	0.0681	1.618	6.48
	40	1.89	0.0705	1.649	6.17
	50	1.94	0.0978	1.492	6.47
	60	2.11	0.1110	1.455	6.38

ΔH of initial pH 4 and pH 10 are equal to 2.504 and 3.580 kcal/mol, respectively.

REFERENCES

- J. M. Randall, W. Reuter, and A. C. Waiss, *J. Appl. Polym. Sci.*, **19**, 1563 (1975).
- J. M. Randall, E. Hautala, and G. McDonald, *J. Appl. Polym. Sci.*, **22**, 379 (1978).
- P. Kuman and S. S. Dara, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 397 (1981).
- M. Friedman, C. S. Harisen, W. H. Ward, and H. P. Lundgsen, *J. Appl. Polym. Sci.*, **17**, 377 (1973).
- M. Friedman and M. S. Masri, *J. Appl. Polym. Sci.*, **18**, 2367 (1974).
- M. Friedman and M. S. Masri, *Environ. Sci. Technol.*, **7**, 951 (1973).
- M. Friedman and A. C. Waiss, Jr., *Environ. Sci. Technol.*, **6**, 451 (1972).
- E. J. Roberts and S. P. Rowland, *Environ. Sci. Technol.*, **7**, 552 (1973).
- T. S. Sheriff, C. J. Sollars, D. Montgomery, and R. Perry, *ASTM STP*, **1033**, 273 (1989).
- R. E. Wing, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **19**, 847 (1985).
- J. Mohammad and V. Tare, *J. Appl. Polym. Sci.*, **42**, 317 (1991).
- R. E. Wing, W. E. Rayford, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **22**, 1405 (1979).
- W. C. Chan, *J. Appl. Polym. Sci.*, **50**, 1733 (1993).
- W. C. Chan, *Ang. Makromol. Chem.*, **213**, 81 (1993).
- W. C. Chan, *J. Polym. Res.*, **1**, 221 (1994).
- W. C. Chan, *Polym. Intern.*, **38**, 319 (1995).
- A. D. John, *Lnnge's Handbook of Chemistry*, McGraw-Hill Book Company, New York, 1987.
- Y. Shimizu, S. Yamazaki, and Y. Terashima, *Water Sci. Technol.*, **11**, 41 (1992).