Cellulose Acetate: Interactions with Aqueous Phenol and a Transition Temperature of About 20°C

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SYNOPSIS

Sorption of aqueous phenol onto powdered cellulose acetate can be described with the Langmuir equation at phenol concentrations below $0.10M$. Unacetylated hydroxyl groups are probably the primary sites where phenol hydrogen bonds. As the phenol concentration is increased ($> 0.13M$), additional hydrogen bonding may occur with the carbonyl oxygens on the primary acetate groups, followed by secondary acetates and the beta glucosidic oxygens. Sorption at higher concentrations shows a negative slope for the Langmuir equation, perhaps caused by crowding and partial blocking of sites. Extrapolations to higher phenolic concentrations using the equation from the negative slope isotherm and plotting N versus °C reveal two lines with a point of intersection at $0.77M$. Because of the increase slope above $0.77M$, cellulose acetate may be dissolving in phenol. At concentrations below $0.10M$, two processes were identified using a Van't Hoff plot (9.33 ± 0.30) $\times 10^3$ and (-1.36 ± 0.18) $\times 10^3$ J/mol. The initial moisture present in the polymer appears to be an important experimental variable and a transition temperature of 20.1 ± 0.2°C, probably due to polymer swelling, is reported.

INTRODUCTION

To help the United States meet the Colorado River water quality provisions of its treaty with Mexico, the Bureau of Reclamation is constructing a reverse osmosis (RO) desalting plant, at Yuma, Arizona, that uses cellulose acetate (CA) membranes. During proof testing, engineers[1] observed a greater than expected decline in flux (water volume per time per area of membrane), thought to be caused by fouling. Although pretreatment of the feed water[2] reduced the severity of flux declines, the mechanism for the fouling was poorly understood.

This paper presents laboratory results on the first in a series of studies on the interactions of organics with CA. The feed water organic fraction at the desalting facility contains mostly humic materials along with lesser amounts from pollution and halogenated structures from the chlorination pretreatment process.

This study examines phenol because the oxidation of humic substances in water by chlorine results in nonchlorinated substituted aromatics with phenol functional groups.[3] These compounds may cause "loosening" or "compaction" of membranes that relates to salt rejection properties and flux declines. Phenol is the simplest structure in the homologous series of phenols and exhibits the interesting property of negative solute rejection; i.e., the permeate can have higher concentrations of phenol than of the feed by as much as 20%.[4]

THEORY

Langmuir and van't Hoff Relationships

An equation similar to the Langmuir adsorption isotherm can be derived from either kinetic or equilibrium principles that relate hydrogen bonding of phenol to the nonacetylated hydroxyl binding sites on CA:

$$\frac{C}{N} = \frac{C}{N_d} + \frac{1}{KN_d} \tag{1}$$

in which C = equilibrium phenol concentration (M),

N = number of mol of phenol per gram of CA at a given C, N_d = mol of phenol per hydroxyl site needed for hydrogen bond to occur, and K = a binding constant. If this model is valid, experimental data plotted C/N versus C will be linear according to eq. (1).

Most Langmuir adsorption experiments assume that N_d is independent of temperature. This assumption is not valid here because the polymer is located both under the solution and floating on top. The reason for some of the polymer floating is probably due to entrained air. Because the percentage of entrained air relative to "wet" polymer can be expected to vary with temperature, the number of available sites may also vary. (It can be assumed that only the "wet" sites are available for bonding.) Therefore, because both K and N_d are temperature dependent,

$$KN_d = f(T) \tag{2}$$

The van't Hoff equation can be written

$$\frac{d}{dT} \ln\left[\frac{1}{f(T)}\right] = \frac{\Delta H}{RT^2} \tag{3}$$

$$\frac{1}{f(T)} \frac{df(T)}{dT} = \frac{\Delta H}{RT^2} \tag{4}$$

integrating, and assuming ΔH does not change significantly over the temperature limits of the integration, yields the following:

$$\int \frac{1}{f(T)} df(T) = \frac{\Delta H}{R} \int \frac{1}{T^2} dT \tag{5}$$

$$\ln f(T) = -\frac{\Delta H}{RT} \tag{6}$$

$$\ln(KN_d) = -\frac{\Delta H}{RT} \tag{7}$$

Hydrogen Bonding with CA

Although the polymer used for this study is considered a cellulose triacetate, not all the hydroxyl sites are acetylated. The 39.8% acetyl content (based on the bottle assay) is less than the 44.4% theoretical acetyl content of cellulose acetate.

Water is known to form hydrogen bonds with free (nonacetylated) hydroxyl groups present in CA. Vincent et al.[5] showed that water binds to available hydroxyl groups in a primary mode (up to 2 waters per hydroxyl) and secondary mode (up to 7 waters per hydroxyl). The hydrogen bonding mode depends on the distance from the hydroxyl.

In a similar fashion, phenol hydrogen bonds with the hydroxyl groups at various places on CA. Phenol may also form primary and secondary hydrogen bonds with the available hydroxyl groups present. Next, phenol will hydrogen bond with the carbonyl oxygens on the acetates. The primary (1°) acetate located on each glucose unit is the most likely site after hydroxyl because of steric accessibility. Ultimately, phenol bonds to the secondary acetates and the beta glucosidic oxygens on the polymer.

Experimental

Chemicals

Phenol (ACS grade, 99+%) and cellulose acetate (ACS grade, 39.8% acetyl content) were purchased from Aldrich. ACS grade 4-aminoantipyrine, potassium ferricyanide, monobasic potassium phosphate, and dibasic potassium phosphate were used.

Equipment

Five hundred milliliter Erlenmeyers with glass stoppers were used as reactors. Reaction experiments were temperature controlled using a Blue M "Magni Whirl" constant temperature refrigerated bath.

Procedures

Stock phenol solutions were made daily. Five dilutions of the stock solution were prepared using 100 mL volumetric flasks. A 1 mL of K_2HPO_4—KH_2PO_4 buffer was added to each flask to maintain the reaction pH at 6.9–7.0. Prior to thermal equilibration in the water bath, 0.1 mL samples were pipeted from each flask into five additional volumetric flasks for initial phenol concentrations.

The reactors contained known amounts of CA (2–3 g). These reactors were rinsed out with deionized water either before use or the previous night. The reactors were thermally equilibrated in the water bath. After adding the different phenol solutions to their respective reactors, the mixtures were shaken vigorously for about 30 s and then placed in the water bath for at least 4 h (reaction mixtures < 20°C were equilibrated overnight). Completed reaction mixtures were quickly filtered through Whatman No. 41 paper using temperature-equilibrated glassware. After the filtered solutions reached room temperature, 0.1 mL samples were pipeted from each flask into five additional volumetric flasks for phenol concentrations. The 10 resulting flasks (initial and final phenol samples) were analyzed colorimetrically[6] within 2 h.

RESULTS AND DISCUSSION

Reaction Equilibration Time

The determination of the equilibrium concentration, C, requires sufficient reaction time for phenol to bind with the CA. Figure 1 shows equilibrium in less than 1.0 h, so the equilibration time used for the experiments can be considered sufficient.

Surface vs. Bulk Adsorption

The surface area of the CA is 4.45 m^2/g (Ref. 7) according to the method of Brunauer, Emmett, and Teller (BET).[8] This would result in a maximum of 2.21×10^{-5} mol/g, assuming the surface area of phenol is 3.38×10^{-9} m^2 (approximated from density of phenol and Avogadro's number). Because the density of phenol in CA is several orders of magnitude greater than measured BET surface area would suggest (Fig. 2), phenol binding with CA polymer must therefore be considered a bulk rather than a surface process.

Additional evidence of a bulk process was observed during experiments with increasing phenol concentrations. Initially, the reacting CA appears to be similar to an insoluble white powder in water; however, the particles begin to aggregate as phenol concentration increases. Finally, enough phenol can be added to the water–phenol–CA system so that an immiscible, clear, viscous liquid forms on the bottom of the beaker. This observation suggests that phenol penetrates throughout the polymer structural network.

Langmuir Model

Table I data show that the Langmuir equation adequately describes the sorption of phenol on powdered CA at concentrations below 0.1M over about a 60°C temperature range. The correlation coefficient (R^2) range is from 0.93 to 1.00. The variability over the temperature range of N_d and K may be caused by a complex relationship between the ratio of air-entrained polymer to "wet" polymer versus temperature of the solution.
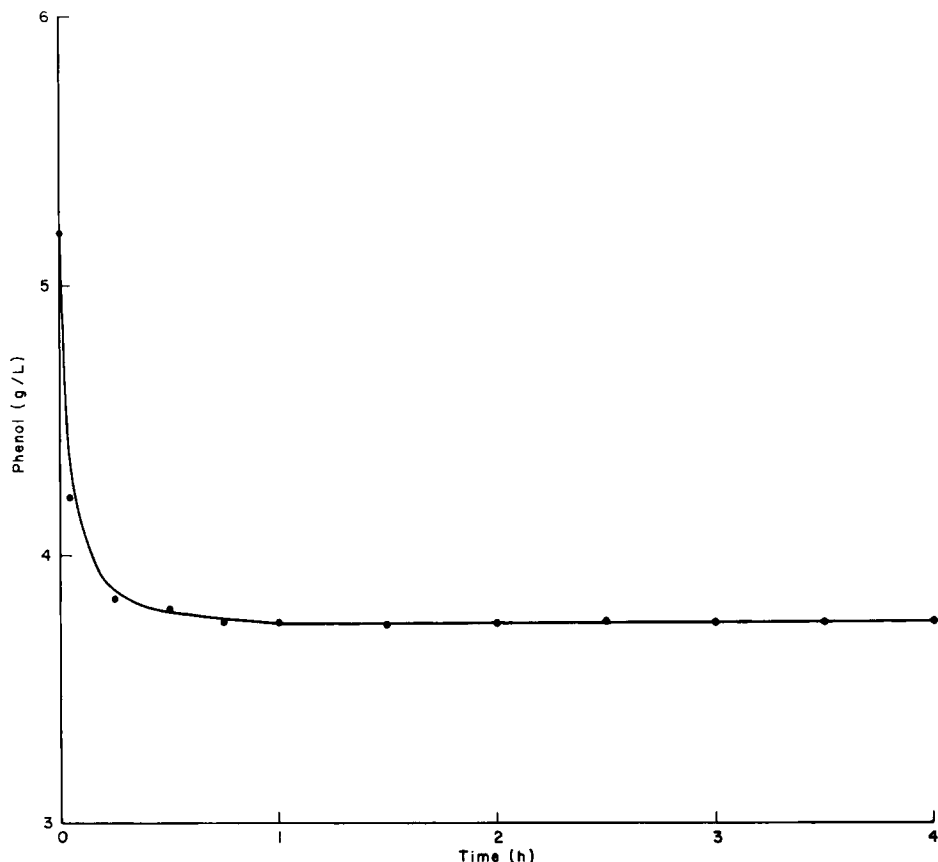

Figure 1   Equilibration time required for phenol and cellulose acetate in water at 25°C.

Table I The Langmuir Model for the Cellulose Acetate/Air/Aqueous Phenol System

Temp (°C)	Sample Size (n)	Binding Sites/g $[N_d\ (\times 10^{-3})]$	Binding Constant (K)	Correlation Coefficient (R^2)
5.0	4	4.39	5.13	1.00
12.4	5	2.33	11.1	0.98
18.7	4	3.53	6.53	0.99
20.4	5	2.77	8.42	0.95
22.7	5	3.19	7.01	0.94
30.7	5	2.16	11.1	1.00
33.5	5	2.45	8.16	0.95
34.4	5	3.05	6.45	1.00
34.4	5	2.81	8.43	1.00
41.6	4	2.53	9.48	0.99
43.8	4	3.26	5.25	0.99
47.1	4	3.41	4.95	0.97
48.5	5	2.89	5.69	0.94
63.8	4	2.16	6.78	0.99

CA-Phenol Hydrogen Bonding

At lower phenol concentrations ($< 0.1M$), phenol is probably hydrogen bonding with CA primarily at the free hydroxyl groups on the CA polymer. Increasing the concentration of phenol saturates available hydroxyl groups and may lead to hydrogen bonding with the carbonyl oxygens of the acetate groups and the glucosidic oxygens. Also, greater concentrations of undissociated phenol exist for hydrogen bonding to these sites at higher total phenol concentrations.

Figure 2 shows that a linear relationship for N versus C is maintained even with increased phenol concentrations. Figure 3(a) shows these same data plotted as C/N versus C. This shift to new sites is seen in Figure 3(a), where the point of intersection at $0.13M$ suggests hydrogen bonding with the carbonyl oxygens of the acetate groups and glucosidic oxygens.

A new Langmuir model with a negative slope [Fig. 3(a)] is observed at concentrations greater than $0.13M$. The negative slope may be caused by steric crowding by bound phenol and/or the CA polymer itself. The primary ($1°$) acetate group on each glucose unit can hydrogen bond with phenol with little hindrance. However, the secondary acetates and glucosidic oxygens would be sterically hindered.

Additional phenol can weaken the polymer structure as phenol dissolves the CA. If the equation for the negative slope [Fig. 3(a)] is used to extrapolate the C versus N data, Figure 3(b) results with two lines and a point of intersection at $C = 0.77M$. The increase in the slope beyond the point of intersection may be caused by phenol dissolving CA.

Two Processes

One of the more interesting and unanticipated results of this study can be seen in the van't Hoff plot (Fig. 4) of Table I data. The two slopes, suggesting two processes, were not anticipated. The enthalpy change (ΔH) and standard error for the two processes are (9.33 ± 0.30) $\times 10^3$ and (-1.36 ± 0.18) $\times 10^{-3}$ J/mol of phenol sorbed.[8] Data collected on successive days would randomly follow one process or the other.

Careful drying of wet polymer over calcium sulfate at 10°C and 30°C (chosen since they are above and below the 20°C transition temperature shown in Fig. 4) showed no difference in final mass to support a hypothesis that "bound" versus "associated" water may cause the observed difference. No drying rate changes corresponding to the loss of the two differently bound waters were observed. Similarly, "switching" of processes was not observed to be caused by different initial temperatures of the polymer, different reactor materials, the degree of mixing, or other experimental artifacts.

Finally, after carefully reviewing the experimental procedure, I realized that the two processes may be related to swelling of the polymer reactant from exposure to residual rinsing water left in the reactor. Polymer was weighed into either dried glass reactors (rinsed out in deionized water the day before) or wet reactors containing around 0.5 mL of water (rinsed out before use).

I determined that CA powder changes density from 0.456 g/L "as is" from the bottle to 0.434 g/L after exposure to moist air for 3 weeks at 25°C. This experiment was performed in a glass desiccator
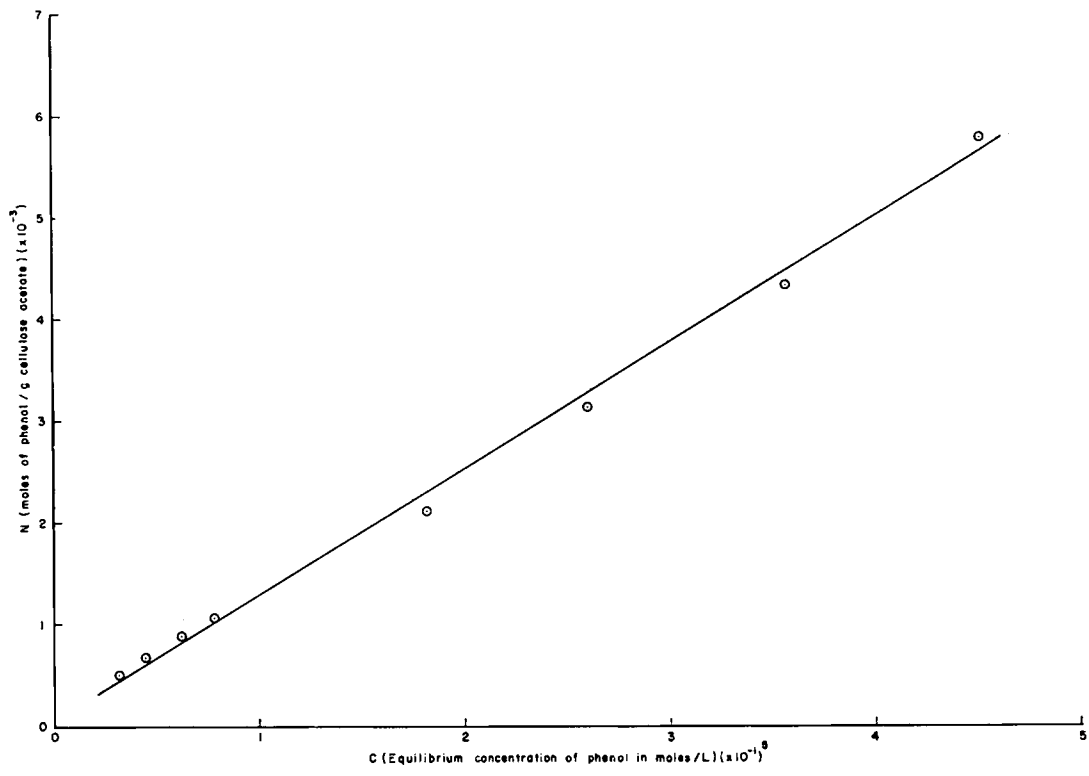
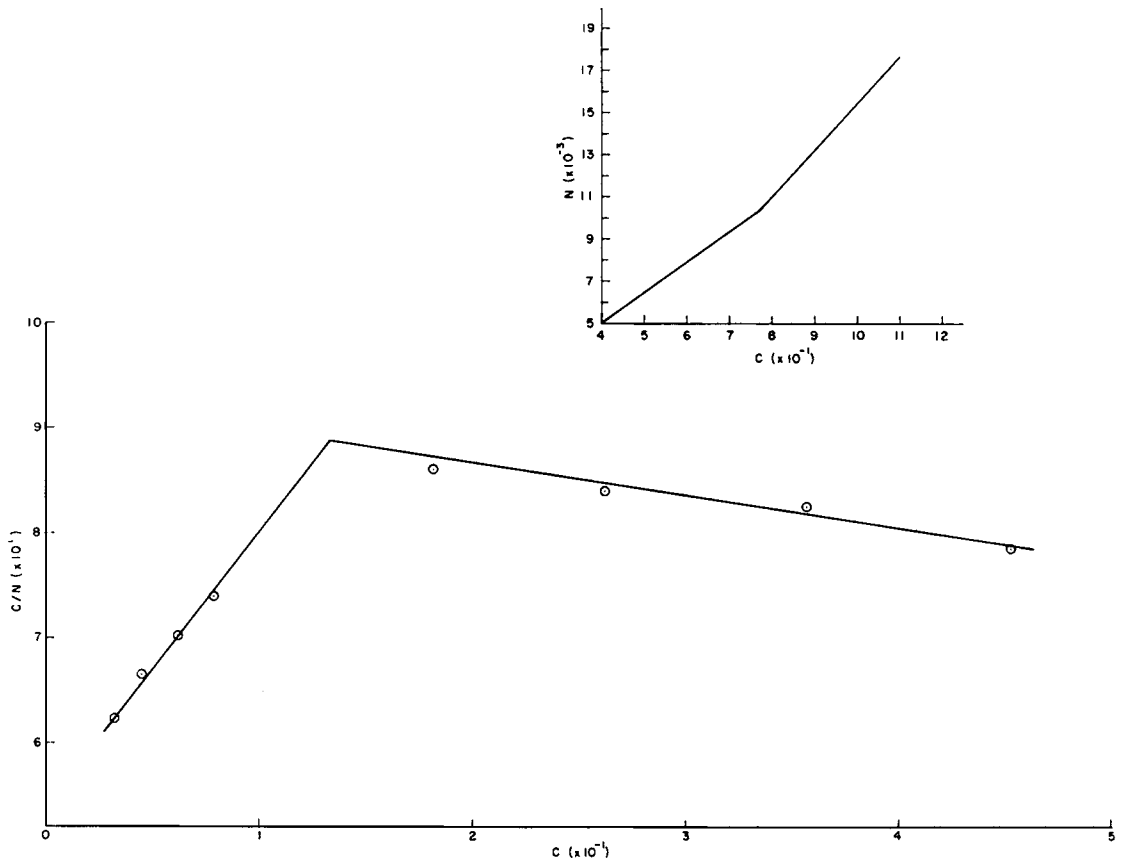**Figure 2**   The adsorption of phenol by cellulose acetate in water at 25°C.

Figure 3   (a) Langmuir relationship satisfied in two concentration regions; (b) extrapolation to higher phenol concentrations showing CA dissolving in phenol.
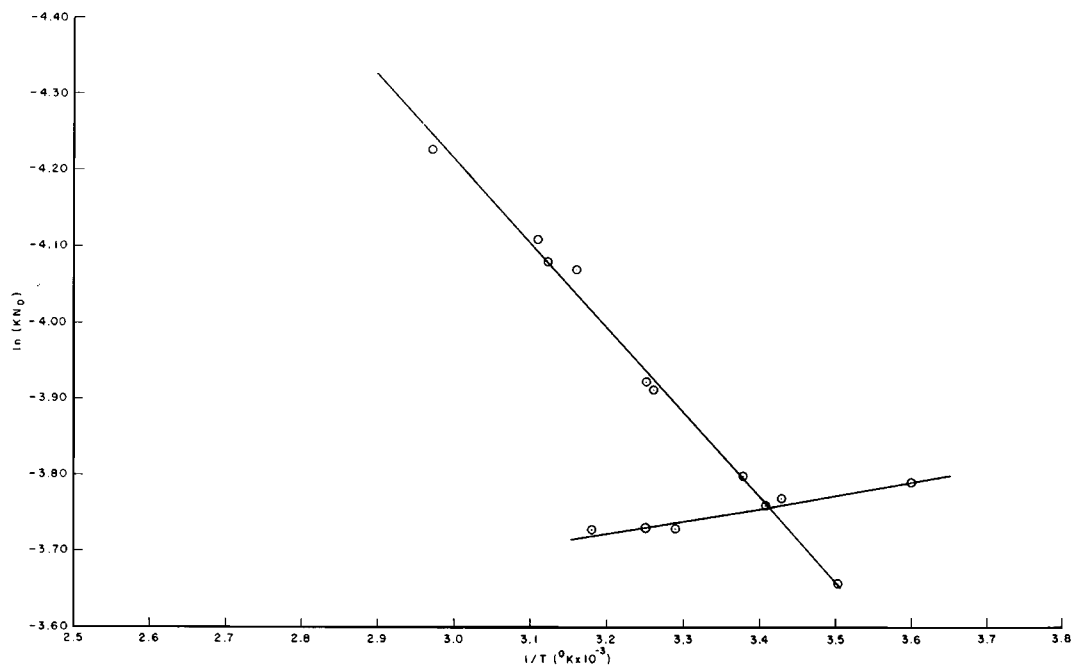
Figure 4 Van't Hoff plot showing two processes and transition temperature for aqueous phenol and CA.

with a beaker of CA powder partially immersed in 3 cm of water. Microscopic examination also revealed swelling of individual particles on exposure to moist air. Swelling was also observed on CA exposed to moist air at 30°C but not for CA exposed to moist air at 10°C. The explanation for the swelling seems to be that small amounts of water present in

the CA can hydrogen bond with the polymer, causing the polymer structure to expand (Table II).

Thus, when moist polymer comes in contact with phenol, the phenol displaces this water and hydrogen bonds on these sites. This is an exothermic reaction shown by the positive slope in Figure 4.

If the polymer has no initially added water, then the phenol must do mechanical work expanding the polymer. Therefore, this is an endothermic process (negative slope in Fig. 4).

The transition temperature and standard error[9] identified in this work is 20.1 ± 0.2°C and is similar to what has long been known about cellulose by Wahba et al.[10] Their "on or about 25°C" temperature transition for cellulose is similar to results reported here for CA. The explanation for the phenomenon might be similar, too. Perhaps, below the transition temperature, water is unable to expand the polymer structure and hydrogen bond with the free hydroxyl groups present.

Table II Aqueous Phenol and CA Tests at 34.4°C or 3.25 × 10⁻³ K⁻¹: Moisture the Determining Factor

ln (KN_d)	T (°C)[a]	Condition[b]
3.77	34.4	5 mL of H_2O added before phenol
3.74	5.0	5 mL of H_2O added before phenol
3.79	34.4	5 mL of H_2O with different reactor
3.78	25.0	0.5 mL of H_2O added before phenol
3.69	5.0	0.5 mL of H_2O added before phenol
3.90	25.0	Dry
3.93	5.0	Dry
3.91	5.0	Dry
3.95	34.4	Dry, different reactor
3.96	25.0	Dry, fast mixing with phenol solution
3.93	25.0	Dry, slow mixing with phenol solution

[a] Initial temperature of polymer prior to the addition of any liquid.
[b] Water temperature at 25°C.

CONCLUSION

The Langmuir equation seems to describe the process of phenol sorption by CA at concentrations below $0.1 M$ over the temperature range from about 5 to 65°C. The process probably consists of phenol hydrogen bonding with the free hydroxyl groups on

the polymer. With higher concentrations of phenol ($> 0.13 M$), a transition occurs, perhaps caused by saturation of available sites and subsequent hydrogen bonding with the carbonyl oxygens of the acetate groups and beta glucosidic oxygens. This previously unreported transition obeys a different Langmuir equation with a negative slope.

Steric hindrance is thought to cause this behavior by crowding and partial blocking of binding sites as more phenol binds. Extrapolation to higher concentrations suggests a point of intersection near $0.766 M$, with the increasing slope above this concentration. This behavior is believed to be caused by phenol dissolving in the polymer.

The transition temperature of $20.1°C$ may result from water molecules hydrogen bonding at the hydroxyl sites of the polymer. At temperatures below $20.1°C$, water does not have sufficient kinetic energy to cause expansion of the CA polymer leading to formation of hydrogen bonds.

ADDITIONAL STUDIES

The transition temperature identified in this paper should be investigated with other techniques. Various properties such as the heat of wetting, water sorptivity, specific volume, refractive index, and modulus elasticity might give additional evidence for this transition temperature.

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