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Effect of Temperature on Equilibrium Adsorption of Phenols onto Nonionic Polymeric Resins

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ABSTRACT

The amounts of equilibrium adsorption of phenol and 4-chlorophenol from aqueous solutions on nonionic polymeric resins were measured in the 288–318 K temperature range. In general, these polymeric resins have a higher capacity for 4-chlorophenol at low solute concentrations but for phenol at higher solute concentrations. The adsorption data for both phenols were presented in terms of the number of adsorbed monolayers and the fraction of pore volume filled due to poor fit by the widely used Langmuir, Freundlich, and BET equations over the entire concentration range (100–3000 g/m^3). Finally, the isosteric enthalpies of adsorption were determined. They decreased with increasing surface coverage.

Key Words. Equilibrium adsorption; Phenol; 4-Chlorophenol; Nonionic polymeric resins; Temperature effect

INTRODUCTION

Phenol and its derivatives are versatile raw materials and/or organic solvents used in petroleum and other chemical industries. However, most phenols are extremely toxic at the concentrations discharged into the receiving effluents. Increasing concern for public health and environmental quality has led to the establishment of limits on the acceptable environmental levels of specific pollutants. Thus, the removal or destruction of phenols from such streams has become a major environmental problem (1).

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Liquid-phase adsorption is effective for the collection of suspended solids, odors, organic matter, and oils from aqueous streams. Activated carbon is the most widely used adsorbent for this purpose. In recent years, nonionic polymeric resins have been increasingly viewed as an alternative to activated carbon for the removal of organic pollutants from waste streams. Earlier studies demonstrated that, on a mass basis, polymeric resins have a lower adsorption capacity for most organic species than does activated carbon (2); however, they are able to selectively remove low molecular weight organic species (3). The wide variations in functionality, surface area, and porosity available for polymeric resins present the possibility of customizing resins for the selective removal of specific organic species (4, 5). Furthermore, regeneration of polymeric resins can easily be accomplished with a solvent (6), while a high temperature and/or stream is needed for the regeneration of activated carbon (7).

A large number of equilibrium studies have been made for the adsorption of phenols on commercial or synthetic nonionic polymeric resins (8–20). In this study we focused on the influence of temperature on liquid-phase adsorption of phenol and 4-chlorophenol on three Amberlite XAD resins. The isosteric enthalpies of adsorption were evaluated in order to compare them with those found in the literature.

EXPERIMENTAL

Resins, Reagents, and Solutions

Three nonionic polymeric resins (Amberlite XAD-4, XAD-7, and XAD-16) were purchased from Rohm and Haas Co. Their physical properties, which were mostly supplied by the manufacturer, are compiled in Table 1. Prior to

TABLE 1
Physical Properties of the Polymeric Resins Obtained from the Manufacturer

Property	XAD-4	XAD-7	XAD-16
Structure	Aromatic, styrene-divinylbenzene	Aliphatic, methyl methacrylate	Aromatic, divinylbenzene
Hydrophobicity	Hydrophobic	Moderately polar	Hydrophobic
BET surface area (m^2/g)	750	450	860
Mean pore diameter (nm)	5	9	9
Pore volume (cm^3/g)	0.974	1.140	1.404
Porosity (cm^3/cm^3)	0.547	0.532	0.550
Particle size (wet mesh)	20–50	20–50	20–50
Swelling ratio:[a]			
In water	1.02	1.14	1.02
In phenol (88 wt%)	1.18	1.20	1.22

[a] Taken from reference 13.

use as adsorbents, they were washed with deionized water (Millipore Milli-Q) several times to remove inorganic impurities, such as Na_2CO_3 and NaCl, until the rinse solutions became clear. These resins were then washed with acetone and *n*-hexane several times, and rinsed for 12 hours to remove organic impurities such as alkylbenzenes, styrene, and biphenyls. Finally, they were dried at 323 K in a vacuum for 2 hours.

The aqueous solutions were prepared by dissolving analytical-grade phenol or 4-chlorophenol (Merck) in deionized water without pH adjustment. The solution pH did not change significantly during adsorption. It was 6.77–6.80 for phenol and 6.68–6.77 for 4-chlorophenol in the whole concentration range studied (<3000 g/m^3). Because the solution pH was much less than the pK_a (Table 2), both phenols are assumed to exist predominantly in their undissociated forms.

Adsorption Equilibrium Experiments

A fixed amount of dry resin (0.1 g) and 0.1 dm^3 of an aqueous phase were placed in a 0.25-dm^3 glass-stoppered flask and shaken at 130 rpm for 3 days using a thermostated shaker bath (Firstek Model B603, Taiwan). Preliminary experiments had shown that the adsorption studied was complete after 1 day. After equilibrium, the aqueous pH was measured by a Horiba pH meter (Model F-23) and the concentrations of phenol and 4-chlorophenol were analyzed using an UV/visible spectrophotomer (Jasco Model U-551) at a wavelength of 270 and 280 nm, respectively. Each experiment was duplicated under identical conditions. The resin-phase concentration of solute, q_e (mol/kg), was calculated according to

$$q_e = V(C_0 - C_e)/W \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations (mol/m^3), respectively, V is the volume of solution (m^3), and W is the weight of dry resins (kg).

TABLE 2
Physical Properties of the Solutes

Solute	Surface area (m^2/molecule)[a]	Density (g/cm^3)	Aqueous solubility (mg/dm^3)	pK_a (298 K)[b]
Phenol	3.05×10^{-19}	1.057 (314 K)	87,000 (298 K)	9.86
4-Chlorophenol	3.26×10^{-19}	1.265 (298 K)	26,000 (298 K)	9.41

[a] Taken from reference 13.

RESULTS AND DISCUSSION

Equilibrium Adsorption

In this study, solute adsorption is expressed in terms of the number of equivalent surface monolayers (θ), which is defined as (13)

$$\theta = q_e N_A \sigma / A_s \tag{2}$$

where σ is the surface area of an adsorbed molecule (m^2/molecule), N_A is Avogadro's number, and A_s is the specific surface area of the resin (m^2/g). The values of A_s and σ are given in Tables 1 and 2. The relationships between θ and the liquid-phase equilibrium concentration (C_e) at different temperatures and polymeric resins are shown in Figs. 1–3. Basically, they are equivalent to conventional isotherm plots, that is, q_e vs C_e.

The adsorption data are frequently quantified via a theoretical or empirical isotherm equation because it describes how the solutes interact with adsorbents and so is critical in optimizing the use of adsorbents. It is evident from Figs. 1 and 2 that the Langmuir and Freundlich equations are inapplicable to the present cases over the whole concentration range, as reported previously (19). The two-parameter BET equation was also tested. The fit is not good, es-

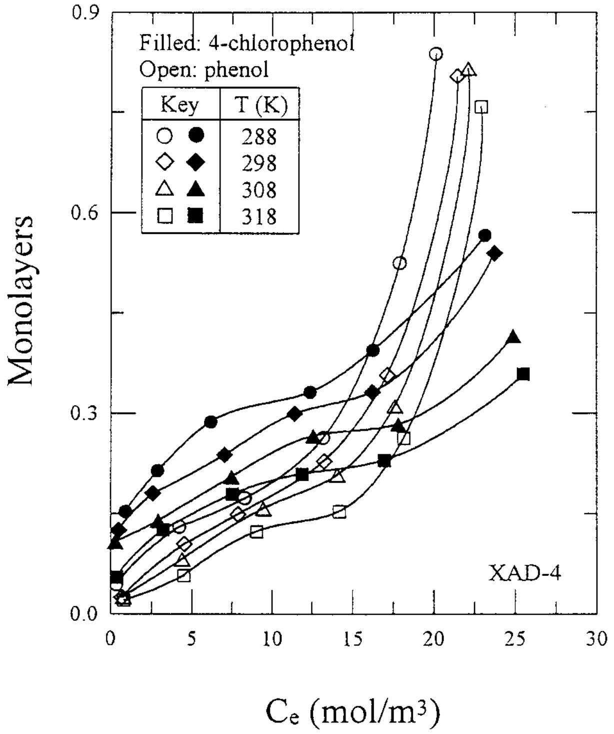

FIG. 1 Adsorption monolayers of phenols on XAD-4 at different temperatures.

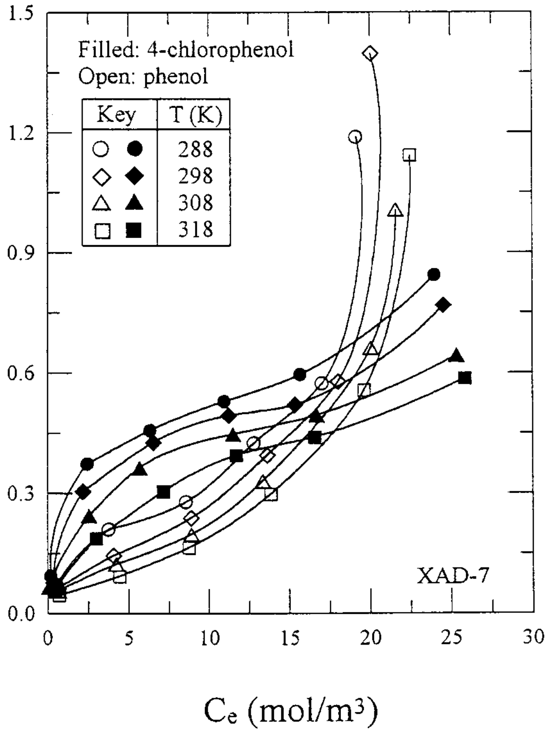

FIG. 2 Adsorption monolayers of phenols on XAD-7 at different temperatures.

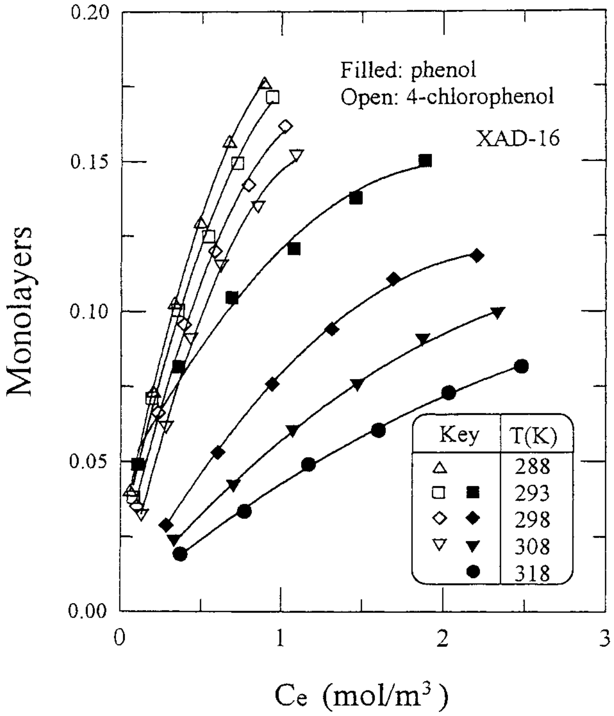

FIG. 3 Adsorption monolayers of phenols on XAD-16 at different temperatures.

pecially for 4-chlorophenol; for example, the correlation coefficients of the linearized plots at different temperatures locate within 0.91–0.98 (phenol/XAD-4), 0.89–0.95 (phenol/XAD-7), 0.60–0.83 (4-chlorophenol/XAD-4), and 0.63–0.86 (4-chlorophenol/XAD-7). Gusler et al. (13) also demonstrated the inapplicability of conventional two-parameter isothermal equations to similar adsorption systems. The reason given was that conventional equations are applicable only for monolayer (or close to) adsorption, and they observed multilayer adsorption (greater than 10), indicative of a significant amount of a*b*sorption contribution to the solute uptake. As we will see in the following section, the contribution of the a*b*sorption process is negligible here. Such discrepancies may result from different methods of resin preparation. In the work of Gusler et al. (13), after wetting the resins with acetone they were rinsed with water until the UV spectrum of rinse water showed no absorbance greater than 0.001 unit for the 190–500 nm wavelength range.

Although it was reported that the three-parameter Redlich–Peterson equation (21) gives a good fit for phenol adsorption from dilute solutions on XAD-4 and XAD-7 (15) as well as on XAD-8 (11), this is not likely to be the case because of the broader concentration range used. Hence, a search for the best fit of isotherm data was not made.

As shown in Figs. 1–3, adsorption ability drops with rising temperature for all the systems studied, indicating the exothermic nature of the adsorption process. For a given XAD-4 or XAD-7 resin, a higher adsorption capacity is obtained for 4-chlorophenol at low C_e but for phenol at C_e beyond 15–20 mol/m^3 (Figs. 1 and 2). This will be the case for XAD-16 (Fig. 3) if the solute concentration range is extended. As expected, the affinity for the more hydrophobic solute 4-chlorophenol on hydrophobic resins is stronger (19), although XAD-7 is moderately polar. Actually, the adsorption data at low C_e ($<$15 mol/m^3) are fit by the Langmuir equation in this work. The adsorption equilibrium constant (K_L) for 4-chlorophenol is about 2–4 times greater than that for phenol under similar conditions, which may provide a quantitative basis for comparison of affinity because K_L is known as a binding constant. A satisfactory explanation for the reversal of adsorption capacity at high C_e cannot be given, although this phenomenon was also reported earlier (13).

Compared to XAD-4, XAD-7 gives a slightly larger amount of adsorption (q_e) for both phenols. Because the specific surface area of XAD-7 is much smaller than that of XAD-4 (Table 1), the adsorption of phenols on XAD-7 is more efficient and the adsorption pattern should be significantly different. Such findings are identical to those reported earlier (19). This reflects the fact that phenol adsorption on XAD-7 exceeds a monolayer at C_e = 20 mol/m^3 (Fig. 2). The ester linkages of XAD-7 provide sites for hydrogen bonding, which explains the higher affinity of phenol relative to XAD-4 (18, 20).

On the other hand, hydrophilic resins such as XAD-12 (nitrosopolystyrene crosslinked with divinylbenzene), Reillex-425 (polyvinylpyridine), and XAD-8 (similar to XAD-7) indicate phenol adsorption exceeding a monolayer at $C_e = 0.6$, 2, and 8 mol/m^3, respectively. Moreover, phenol adsorption on XAD-12 and Reillex-425 reaches 75 and 50 monolayers at $C_e = 850$ and 615 mol/m^3, respectively (13). Owing to their relatively small surface areas, i.e., 22 (XAD-12), 90 (Reillex-425), and 140 m^2/g (XAD-8), it is deduced that the number of available active sites plays an important role in adsorption phenomena. In addition to this, the chemical nature of the resins or the presence of some functional groups also plays an important role; for example, hydrogen bonding at tertiary nitrogen sites of poly(vinylpyridine) is the dominant mechanism of adsorption of phenols (13). Finally, XAD-16, which is made of divinylbenzene, is primarily hydrophobic, but the adsorption data (Fig. 3) lies between those of the hydrophobic (XAD-4) and the hydrophilic resins (XAD-7). For example, phenol adsorption on XAD-16 exceeds a monolayer at $C_e =$ 160 mol/m^3 (13).

Contribution of Solute A*b*sorption

As stated above, the formation of multiple layers on the resin surface reaches 50 or more layers. This is unrealistic because solute–surface interactions are unlikely to extend beyond a few monolayers. Gusler et al. (13) indicated that the uptake of organic solutes on specific polymeric resins may not be due only to surface adsorption but also to solute a*b*sorption (i.e., penetration into the resin matrix). The existence of a*b*sorption is justified by one of the following facts: 1) amount of adsorption in excess of the total pore volume, 2) solute-dependent limiting adsorption volume in the Polanyi potential theory, and 3) relatively high degree of resin swelling in water or concentrated aqueous solute solutions. To check the possibility of solute a*b*sorption in the present cases, the fraction of the pore volume filled (F_p) is calculated (13) by

$$F_p = \frac{[C_0 V - C_e (V - W V_p)]}{\rho V_p} \tag{3}$$

where V_p is the specific pore volume of the resins (m^3/kg) and ρ is the density of the solute (kg/m^3).

Figures 4–6 show these results. Under the conditions examined (concentration range, type of the resins and solutes, and temperature), it is seen that the amount of adsorption does not exceed the total pore volume. In addition, the swelling ratios of the three resins used, defined as the ratio of the volume of the resins immersed in a solvent to that in the dry state, are low (Table 1) compared to the more hydrophilic resins such as XAD-12 and Reillex-425 (13). It is thus considered that the contribution of a*b*sorption to solute uptake is negligibly small.

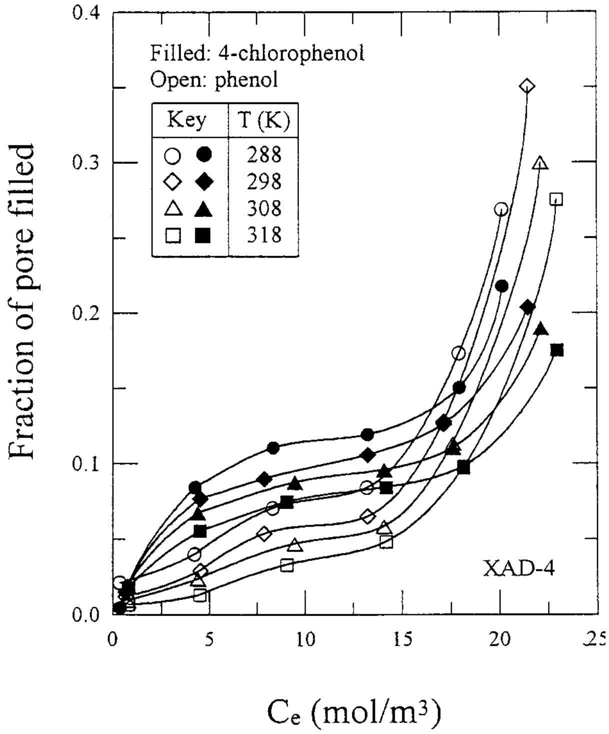

FIG. 4 Fraction of pore volume filled with phenols on XAD-4 at different temperatures.

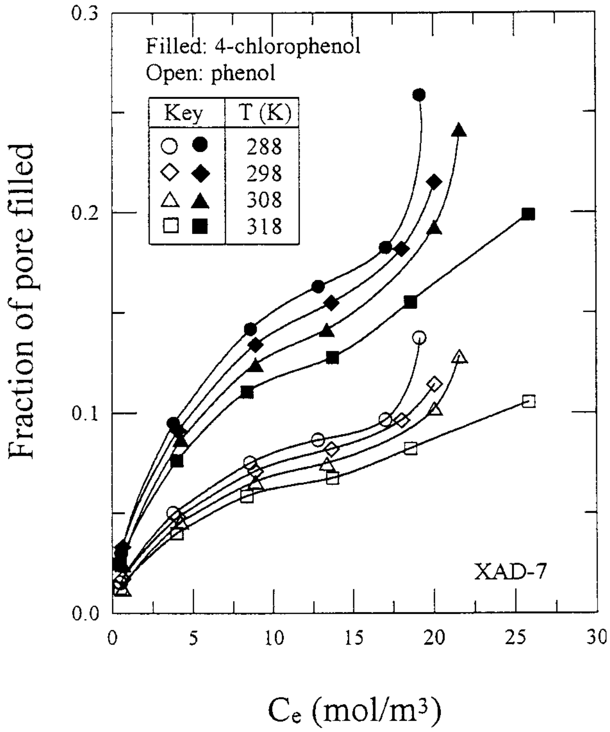

FIG. 5 Fraction of pore volume filled with phenols on XAD-7 at different temperatures.

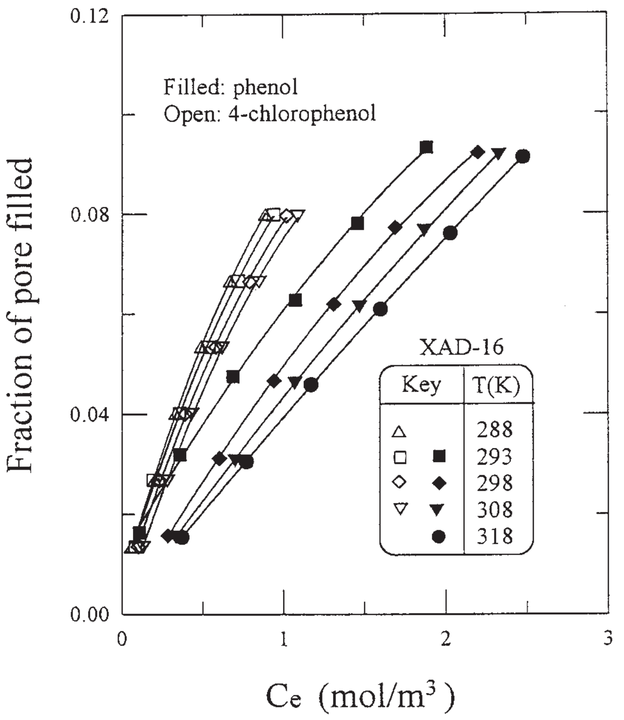

FIG. 6 Fraction of pore volume filled with phenols on XAD-16 at different temperatures.

Isosteric Enthalpy of Adsorption

If all adsorption sites are equivalent, the enthalpy of adsorption will be independent of surface coverage. This is the assumption of the Langmuir equation and, as stated above, this is not true for the present cases. Hence, in the absence of solute a*b*sorption, the isosteric enthalpy of adsorption (i.e., constant θ), ΔH_{ads}, is alternatively evaluated by

$$\left[\frac{d(\ln C_{\mathrm{e}})}{d\,(1/T)}\right]_{\theta} = \frac{\Delta H_{\mathrm{ads}}}{R} \tag{4}$$

Figures 7–9 show the results, where the values of C_{e} at constant θ are obtained from Figs. 1–3. These plots give good linear relationships, and the values of ΔH_{ads} are listed in Table 3. As expected, they decrease with increasing θ, meaning that the active sites on the resin surface are not energetically equivalent and those with greater binding energy are occupied first.

As clearly shown in Table 3, the enthalpies evolved during adsorption are less than about 40 kJ/mol, which agree with those observed for phenol adsorption on polymeric resins as determined by conventional methods (11, 16, 19). However, these values are lower than those obtained for the adsorption of organic solutes on activated carbon materials (22). It is noticed that solute adsorption on activated carbon barely exceeds a monolayer (13), although it has

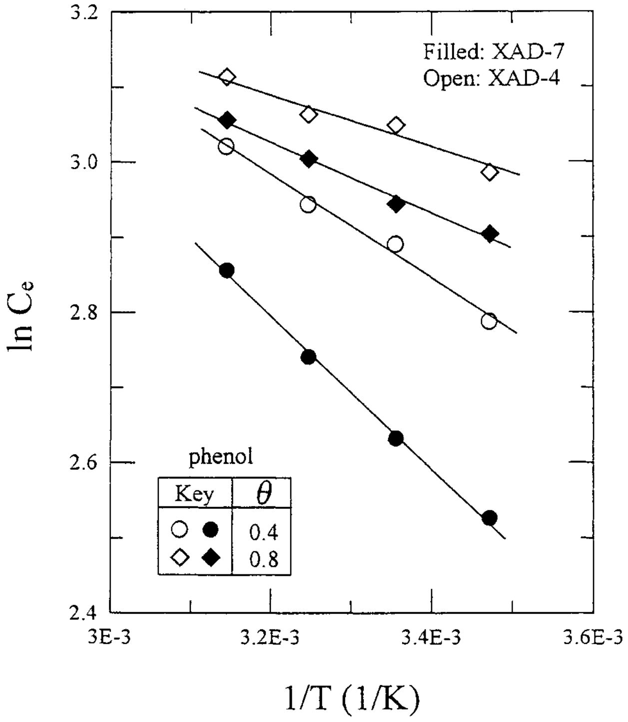

FIG. 7 Determination of isosteric enthalpy of adsorption of phenol on XAD-4 and XAD-7.

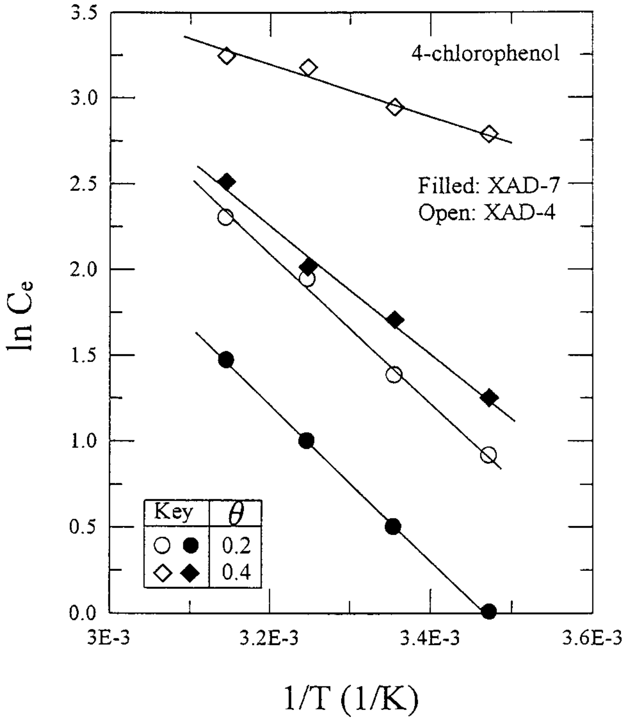

FIG. 8 Determination of isosteric enthalpy of adsorption of 4-chlorophenol on XAD-4 and XAD-7.

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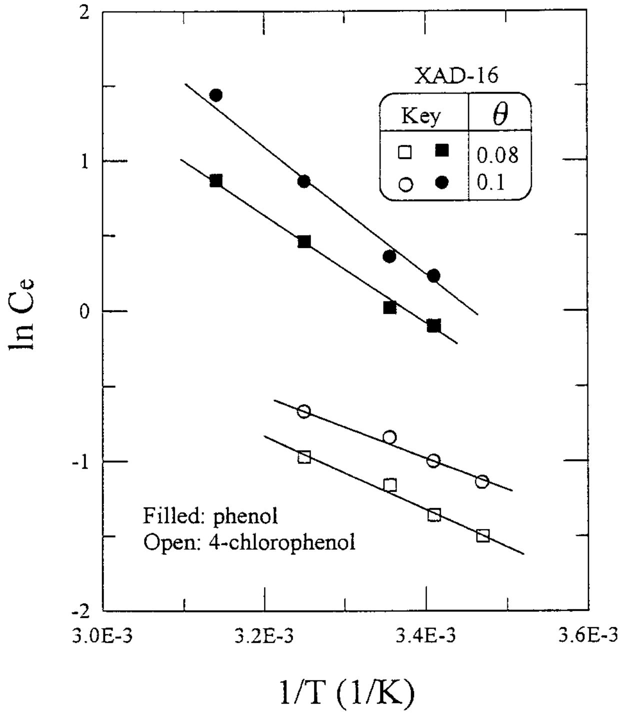

FIG. 9 Determination of isosteric enthalpy of adsorption of phenols on XAD-16

a strong adsorption bond relative to nonionic polymeric resins. In contrast to XAD-4, the slightly higher enthalpy change for XAD-7 confirms its stronger affinity with both solutes, as was discussed above. Moreover, the higher enthalpy of 4-chlorophenol adsorption on XAD-4 and XAD-7 indicates a stronger binding tendency compared to phenol. In summary, the present rigid results on temperature dependence show the uptake of both phenols on nonionic polymeric resins to be a type of physical adsorption.

TABLE 3
Isosteric Enthalpy of Adsorption ΔH_{ads} (kJ/mol) Evaluated at Different Surface Coverages in the Temperature Range 288–318 K

		Monolayer (θ)				
Solute	Resin	0.08	0.1	0.2	0.4	0.8
Phenol	XAD-4		−11.3	−4.98	−2.53	−1.41
	XAD-7		−16.4	−12.5	−3.65	−1.68
	XAD-16	−40.1	−36.0			
4-Chlorophenol	XAD-4		−29.5	−21.3	−8.02	
	XAD-7		−32.8	−21.5	−17.8	
	XAD-16	−21.2	−17.9			

CONCLUSIONS

The use of Amberlite XAD-4, XAD-7, and XAD-16 for the adsorption of phenol and 4-chlorophenol from water has been investigated. The following results were obtained.

1. The isotherm data cannot be satisfactorily fitted by conventional Langmuir, Freundlich, BET, and Redlich–Peterson equations over the whole concentration range (<3000 g/m^3).
2. The adsorption capacity for the more hydrophobic 4-chlorophenol is higher. In contrast to XAD-4, the high specific amount of phenol adsorption on XAD-7 is attributed to the presence of sites for hydrogen bonding provided by the ester linkages of XAD-7. This indicates that phenol adsorption on XAD-7 exceeds a monolayer at relatively low C_e (20 mol/m^3). In addition to the hydrophobicity and chemical nature of the resins, the number of available active sites plays an important role in the adsorption mechanism of organic materials.
3. The contribution of a*b*sorption to solute uptake is negligible under the ranges studied because the uptake does not exceed the total pore volume and the swelling ratios of the three resins in water are low.
4. The isosteric enthalpy of adsorption provides a quantitative basis to determine binding affinity between phenols and the resins. Based on the enthalpy changes (<40 kJ/mol), the uptake of phenols on nonionic polymeric resins is a type of physical adsorption.

NOMENCLATURE

A_s	specific BET surface area of polymeric resins (m^2/g)
C_e	liquid-phase solute concentration at equilibrium (mol/m^3)
C_0	initial solute concentration in the aqeous phase (mol/m^3)
F_p	fraction of pore volume filled
ΔH_{ads}	isosteric enthalpy of adsorption (kJ/mol)
N_A	Avogadro's number
R	universal gas constant (J/mol·K)
q_e	amount of phenols adsorbed at equilibrium (mol/kg)
V	volume of the solution (m^3)
V_p	specific pore volume of the resins (m^3/g)
W	weight of the dry resins (kg)

Greek Letters

ρ	density of the solute (g/cm^3)
θ	number of monolayers
σ	surface area of an adsorbed molecule (m^2/molecule)

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REFERENCES

1. C. C. Lee and Y. Ku, *Sep. Sci. Technol.*, *31*, 2551 (1996).
2. I. H. Suffet, L. Brenner, J. T. Coyle, and P. R. Cairo, *Environ. Sci. Technol.*, *12*, 1315 (1978).
3. G. A. Junk, in *Organic Pollutants in Water. Sampling, Analysis, and Toxicity Testing* (Advances in Chemistry Series 214; I. H. Suffet and M. Malaiyandi, Eds.), American Chemical Society, Washington, DC, 1987, pp. 201–246.
4. P. Cornel and H. Sontheimer, *Chem. Eng. Sci.*, *41*, 1791 (1986).
5. R. Kunin, *Polym. Eng. Sci.*, *17*, 58 (1977).
6. T. M. Grant and C. J. King, *Ind. Eng. Chem. Res.*, *29*, 264 (1990).
7. P. R. Cairo, J. T. Coyle, J. T. Davis, H. M. Neukrug, I. H. Suffet, and A. Wickland, *J. Am. Water Works Assoc.*, *74*, 94 (1982).
8. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, *React. Polym.*, *1*, 39 (1983).
9. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, *Ibid.*, *4*, 39 (1985).
10. E. H. Crook, R. P. McDonnell, and J. T. McNulty, *Ind. Eng. Chem., Prod. Res. Dev.*, *14*, 113 (1975).
11. D. S. Farrier, A. L. Hines, and S. E. Wang, *J. Colloid Interface Sci.*, *69*, 233 (1979).
12. S. Goto, M. Goto, and S. Vchiyama, *J. Chem. Eng. Jpn.*, *17*, 204 (1984).
13. G. M. Gusler, T. E. Browne, and Y. Cohen, *Ind. Eng. Chem. Res.*, *32*, 2727 (1993).
14. R. L. Gustafson, R. L. Albright, J. Heisler, J. A. Lirio, and O. T. Reid Jr., *Ind. Eng. Chem., Process Des. Dev.*, *7*, 107 (1968).
15. A. Itaya, N. Kato, and J. Yamamoto, *J. Chem. Eng. Jpn.*, *17*, 389 (1984).
16. N. Kawabata, I. Higuchi, and J. Yoshida, *Bull. Chem. Soc. Jpn.*, *54*, 3253 (1981).
17. B. R. Kim, V. L. Snoeyink, and F. M. Saunders, *J. Water Pollut. Control Fed.*, *48*, 120 (1976).
18. N. Maity, G. F. Payne, and J. L. Chipchoosky, *Ind. Eng. Chem. Res.*, *30*, 2456 (1991).
19. J. Paleos, *J. Colloid Interface Sci.*, *31*, 7 (1969).
20. G. F. Payne and Y. Ninomiya, *Sep. Sci. Technol.*, *25*, 1117 (1990).
21. O. Redlich and D. L. Peterson, *J. Phys. Chem.*, *63*, 1024 (1959).
22. E. Costa, G. Calleja, and L. Marijuan, *Adsorp. Sci. Technol.*, *5*, 213 (1988).
23. E. P. Serjeant and B. Dempsey, *Ionization Constants of Organic Acids in Aqueous Solutions* (IUPAC Chemical Data Series 23), Pergamon Press, New York, NY, 1979, pp. 160 and 190.

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