

LIQUID PHASE ADSORPTION EQUILIBRIUM OF PHENOL AND ITS DERIVATIVES ON MACRORETICULAR ADSORBENTS

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Liquid-phase adsorption equilibria of phenol, *p*-chlorophenol and *p*-cresol for macroreticular polymeric adsorbents, Amberlite XAD-4 and XAD-7, were measured over a wide range of concentration at three temperatures from 273 to 323 K, in order to find an equation which correlates the equilibrium data best. Among the theoretical equations proposed previously in the literature, the equation of Jossens *et al.* derived thermodynamically on the basis of a heterogeneous surface adsorption theory was proved to be most satisfactory over the entire range of concentration. All conditions assumed in the derivation of the equation were found to be valid. An equation based on the vacancy solution theory gave a fairly good representation. The equations proposed by Okazaki *et al.* and Toth, respectively, were not applicable to the present cases. The equilibrium data were also correlated by an adsorption potential theory, which enables us to predict the adsorption isotherm at different temperatures.

Introduction

Macroreticular polymeric adsorbents (MR resins) have been used for a specific adsorption application, such as recovery and purification of materials,⁶⁾ because they adsorb many water-soluble organic compounds from aqueous solutions and can be easily regenerated by selecting appropriate elution solvents.

Information on adsorption equilibrium is essential to practical adsorption operation. However, there are few systematic studies of equilibrium of adsorption onto MR resins over a wide range of concentration at different temperatures. Hines *et al.* have investigated the applicability of a Redlich-Peterson equation and an adsorption potential theory to adsorption equilibria of phenol on Amberlite XAD-8¹⁾ and of carboxylic acids on Amberlite XAD-2,⁴⁾ respectively. But only the fitting of the experimental data was shown, and no investigation of temperature dependence or thermodynamical soundness of the parameters was made.

In the present work, liquid-phase adsorption equilibria of phenol and its derivatives were measured over a wide range of concentration at three different temperatures using Amberlite XAD-4 and XAD-7 and various isotherm equations were examined to correlate the equilibrium data.

1. Experimental

Two commercial macroreticular resins were used. One is Amberlite XAD-4, a crosslinked styrene-divinylbenzene copolymer which is very hydrophobic. The other is Amberlite XAD-7, a crosslinked polyacrylic ester which is considerably hydrophilic compared with the former. The supplier claimed that the values of surface area of XAD-4 and XAD-7 were 750 and 450 $\times 10^3$ m²/kg, respectively. The resins were washed with a sufficient amount of distilled tetrahydrofuran and methanol until no impurities were detected in the effluents from resin beds by ultraviolet spectrophotometer. Then, methanol in the purified MR resins was replaced with deionized distilled water and they were stored in a desiccator containing water in order to maintain constant moisture content.

Commercial product of specially prepared phenol for chromatography was used without further purification. Commercial products of *p*-chlorophenol and *p*-cresol were used after distillation under reduced pressure. Deionized and further distilled water was used throughout the study.

The concentration of solutions was determined by use of an ultraviolet spectrophotometer (Hitachi type 300).

Adsorption isotherms were determined by a batch method. A certain amount of wet adsorbent was weighed accurately and was put into a flask. Then 5×10^{-5} m³ of solutions containing adsorbates was

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added to the flask. The flasks were sealed, placed on a gyratory shaker and agitated at constant temperature. It was confirmed by following the concentration of solution in the preliminary experiments that adsorption equilibrium of phenol on XAD-7 was attained in about 3 days at 303 K. In the present study, agitation of the flasks was carried out for 6, 7, and 10 days at 323, 303, and 273–278 K, respectively. After that, a sample was taken from each flask by syringe. MR resins were filtered through a stainless steel wire mesh and dried under reduced pressure to determine the dry weight of adsorbents. The experimental data covered the concentration range from 10 to 10^{-2} mol/m³.

2. Results and Discussion

Experimental isotherms for phenol adsorption on XAD-4 and *p*-chlorophenol adsorption on XAD-7 are shown in Figs. 1 and 2, respectively. In all systems, both Freundlich's equation and Langmuir's equation show very poor fit to adsorption data over the entire range of concentration. Therefore, the applicability of empirical or theoretical equations containing three or four adjustable parameters must be investigated. Since we need a theoretical isotherm equation which satisfies thermodynamic boundary conditions at both very low surface coverage and the highest coverage, almost all such equations proposed previously in the literature were examined.

2.1 Equation of Jossens *et al.*

Assuming that an energy distribution function of adsorption sites $f(E)$ obeys Eq. (1), the following relation (Eq. (2)) between an isosteric heat of adsorption E and the amount adsorbed q is derived.⁵⁾

$$f(E) = A(E - E_0)^\alpha \quad (1)$$

$$E_0 - E = Cq^P \quad (2)$$

where E_0 is the maximum isosteric heat of adsorption, P is a constant related to the distribution of energy sites on the surface by the equation $\alpha = (1 - P)/P$, $0 < P < 1$, $A = (P \cdot E_0^{1/P})^{-1}$, and $C = E_0/N_s^P$ (N_s : number of total adsorption sites). Then, the following adsorption isotherm equation is derived.

$$c = (q/H) \cdot \exp(Kq^P) \quad (3)$$

where c is the equilibrium concentration. H corresponds to the Henry's law constant and is related to E_0 as follows.

$$E_0 = -RT^2(d \ln H/dT) \quad (4)$$

K is a function of temperature only:

$$C = -RT^2(dK/dT) \quad (5)$$

These equations have desirable properties. That is, at very low surface coverage, Eq. (3) reduces to

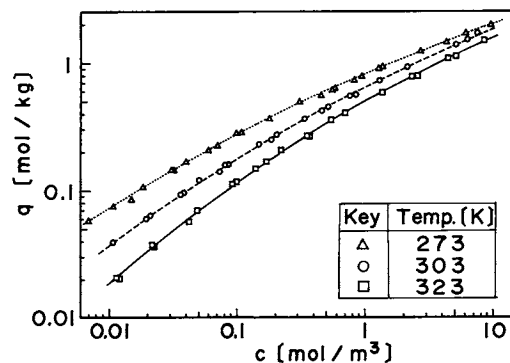


Fig. 1. Adsorption isotherms of phenol on XAD-4. Lines are calculated from equation of Jossens *et al.* —, using three parameters (H, K, P); ---, $P=0.3479$ and two parameters (H, K) shown in Table 1; ·····, $P=0.3479$ and two parameters calculated from equations in Table 2.

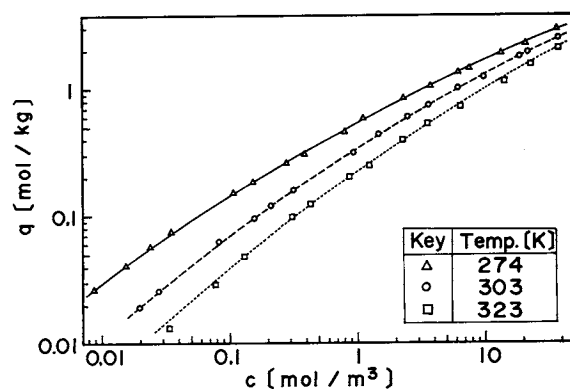


Fig. 2. Adsorption isotherms of *p*-chlorophenol on XAD-7. Lines are calculated from equation of Jossens *et al.* —, using three parameters (H, K, P); ---, $P=0.3453$ and two parameters (H, K) shown in Table 1; ·····, $P=0.3454$ and two parameters calculated from equations in Table 2.

Henry's law for adsorption:

$$\lim_{c \rightarrow 0} q = Hc \quad (6)$$

and at the highest coverage, an ultimate adsorption amount q^∞ can be obtained from Eq. (2), irrespective of temperature.

$$q^\infty = (E_0/C)^{1/P} \quad (7)$$

Therefore, each parameter should satisfy the following thermodynamical conditions: The value of P is characteristic of the adsorbent only, irrespective of both the temperature and the nature of adsorbates. Temperature dependence of H and K must be expressed by Eqs. (4) and (5), respectively. The relation between E and q holds as in Eq. (2).

Jossens *et al.* have found that the isotherm equation (Eq. (3)) gives a good representation of the data for adsorption of phenols and aromatic acids from aqueous solutions on activated carbon at 293 K.⁵⁾ However, because equilibrium experiments were done

only at one temperature and the equilibrium relation did not approach Henry type even in low concentration regions measured, the soundness of the parameters determined is questionable. For example, values of P were not constant for a given activated carbon and showed considerable scatter among adsorbates. Therefore, there remains a problem whether these equations are really applicable. In the present system of MR resins, as shown in Figs. 1 and 2, the equilibrium relation approaches Henry type in low concentration regions, so that the soundness of these equations can be investigated.

Three parameters in Eq. (3) were determined for each system at different temperatures by using a least-squares fitting procedure. Solid lines in Figs. 1 and 2 were calculated from Eq. (3), using the three parameters thus determined. The good fit of the lines to the data shows that Eq. (3) gives a good representation of the data. Considering that the value of P is dependent on the adsorbent only, all values of P determined for the same adsorbent were averaged. Thus, 0.3479 ± 0.0540 and 0.3453 ± 0.0628 are obtained as the value of P for XAD-4 and XAD-7, respectively.

When these averaged values are used, the remaining two parameters, H and K , can be determined. The values of parameters and relative deviations between the calculated and the experimental data are listed in Table 1. Broken lines in Figs. 1 and 2 were calculated from Eq. (3) using the parameters shown in Table 1. As shown in Table 1 and Figs. 1 and 2, Eq. (3) gives a good representation of the present adsorption data over the entire range of concentration. Concerning these adsorbents, Eq. (3) is regarded as an equation containing two adjustable parameters.

As shown in Fig. 3, the temperature dependence of the values of H and K thus determined agrees well with Eqs. (4) and (5), showing that these parameters are reasonable thermodynamically. The values of E_0 and C were determined from slopes based on the corresponding equations and are listed in Table 2. Using these values, q^∞ was calculated from Eq. (7) and its values are also listed in Table 2. It can be said that the values of E_0 and H are in the following order: phenol < p -cresol < p -chlorophenol. This is opposite to the order of solubility of the adsorbates in water. These results show that hydrophobic interaction between the MR resins and adsorbates plays an important role in adsorption on MR resins. Irrespective of adsorbates, the value of q^∞ is about 5.9 and 3.2 mol/kg for XAD-4 and XAD-7, respectively. This seems to correspond to the specific surface area of these adsorbents.

The adsorption isotherms calculated from Eq. (3) with both the fixed value of P and the values of H and K containing the temperature dependence (Table 2)

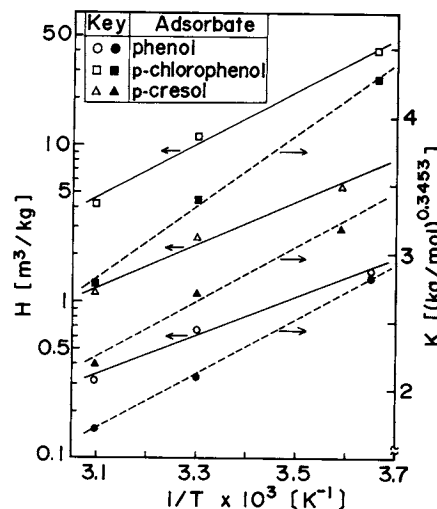


Fig. 3. Dependence of parameters H and K on temperature for XAD-7.

are shown by dotted lines in Figs. 1 and 2. The relative deviations between calculated and experimental data are listed in Table 2. As shown in Table 2 and Figs. 1 and 2, Eq. (3) with the parameters in Table 2 is successful for fitting the present adsorption isotherm over the entire range of concentration at all temperatures.

Using isotherms at different temperatures, values of the isosteric heat of adsorption, E , were obtained at several amounts adsorbed. The isosteric heats of adsorption thus obtained decrease with an increase in the amount adsorbed, as plotted in Fig. 4. This phenomenon is commonly observed for adsorption onto heterogeneous surfaces. The solid lines in Fig. 4 were calculated from Eq. (2) using the values of P , C , and E_0 shown in Table 2. The relative deviations between experimental and calculated values, ΔE , are shown in the last column in Table 2. The deviations are less than 3% except for the XAD-7- p -cresol system. Therefore, it is clear that Eq. (2) is also satisfied by parameters determined from the above-mentioned procedure.

In the present investigation, as mentioned above, it was confirmed that not only does the equation of Jossens *et al.* give a satisfactory representation for adsorption equilibrium from aqueous solutions on MR resins in the concentration range from 10 to 10^{-2} mol/m³ at various temperatures, but also all conditions related to the equation are completely satisfied. That is, the thermodynamical appropriateness of the equation of Jossens *et al.* has been verified experimentally for the first time.

2.2 Equation of Okazaki *et al.*

Okazaki *et al.* have proposed the following equation containing three adjustable parameters: k_{\min} , k_{\max} , and q^∞ .⁸⁾

Table 1. Experimental conditions, and parameters and relative deviations in the equation of Jossens *et al.*

Absorbent	Absorbate	Temp. [K]	c [mol/m ³]	P [—]	H [m ³ /kg]	K [(kg/mol) ^{P}]	Δq [%]*
XAD-4	Phenol	273	$8.35 \times 10^{-3} - 6.86$	0.3479	7.153	3.238	1.93
		274	$8.64 \times 10^{-3} - 36.0$		7.123	3.132	2.74
		303	$1.99 \times 10^{-2} - 36.6$		1.781	2.378	1.48
		323	$3.34 \times 10^{-2} - 36.8$		0.7153	1.986	4.13
	<i>p</i> -Chlorophenol	276	$3.13 \times 10^{-2} - 9.01$		138.4	4.548	1.60
		303	$8.56 \times 10^{-3} - 17.9$		30.88	3.642	1.75
		323	$1.71 \times 10^{-2} - 15.5$		11.78	3.313	2.77
	<i>p</i> -Cresol	274	$1.73 \times 10^{-2} - 7.42$		55.44	3.858	3.64
		303	$1.36 \times 10^{-2} - 13.7$		14.00	3.174	1.50
		323	$1.10 \times 10^{-2} - 26.1$		4.337	2.338	2.05
XAD-7	Phenol	274	$8.37 \times 10^{-3} - 10.7$	0.3453	1.566	2.822	3.48
		303	$9.51 \times 10^{-3} - 10.6$		0.6655	2.095	2.97
		323	$5.21 \times 10^{-2} - 13.8$		0.3149	1.713	3.45
	<i>p</i> -Chlorophenol	273	$6.96 \times 10^{-3} - 9.63$		40.33	4.275	1.82
		303	$1.07 \times 10^{-2} - 7.60$		11.43	3.394	1.93
		323	$1.15 \times 10^{-2} - 8.60$		4.197	2.774	4.00
	<i>p</i> -Cresol	278	$3.14 \times 10^{-2} - 22.2$		5.348	3.183	2.83
		303	$2.29 \times 10^{-2} - 26.9$		2.559	2.705	2.87
		323	$3.02 \times 10^{-2} - 24.8$		1.135	2.187	2.16

$$\Delta q [\%] = (100/N) \sum_i^N (|q_{i, \text{calc.}} - q_{i, \text{exp.}}| / q_{i, \text{exp.}})$$

N = No. of experimental points.

Table 2. Parameters expressing the temperature dependence of adsorption isotherms, ultimate adsorption amount, and relative deviations in the equation of Jossens *et al.*

Adsorbent	Adsorbate	P [—]	K [(kg/mol) ^{P}]	H [m ³ /kg]	C [kJ · kg ^{P} /mol ^{$P+1$}]	E_0 [kJ/mol]	q^∞ [mol/kg]	Δq^* [%]	ΔE^{**} [%]
XAD-4	Phenol	0.3479	$2167/T - 4.742$	$2.548 \times 10^{-6} \exp(4062/T)$	18.01	33.77	6.09	4.09	2.97
	<i>p</i> -Chlorophenol		$2384/T - 4.127$	$6.206 \times 10^{-6} \exp(4672/T)$	19.82	38.84	6.92	3.39	2.82
	<i>p</i> -Cresol		$2657/T - 5.773$	$3.918 \times 10^{-6} \exp(4527/T)$	22.09	37.64	4.63	3.35	1.43
XAD-7	Phenol	0.3453	$2002/T - 4.495$	$5.150 \times 10^{-5} \exp(2838/T)$	16.65	23.59	2.75	6.08	1.59
	<i>p</i> -Chlorophenol		$2627/T - 5.325$	$2.300 \times 10^{-5} \exp(3940/T)$	21.84	32.76	3.24	4.17	2.08
	<i>p</i> -Cresol		$1990/T - 3.934$	$7.908 \times 10^{-5} \exp(3113/T)$	16.54	25.88	3.65	3.78	7.26

* See Table 1.

$$\Delta E [\%] = (100/N) \sum_i^N (|E_{i, \text{calc.}} - E_{i, \text{exp.}}| / E_{i, \text{exp.}})$$

$E_{i, \text{exp.}}$ was obtained at several amounts adsorbed by using isotherms at different temperatures and $E_{i, \text{calc.}}$ was calculated from Eq. (2) with the values of P , C , and E_0 .

$$q = \frac{q^\infty}{\ln(k_{\max}/k_{\min})} \ln \frac{(1 + k_{\max}c)}{(1 + k_{\min}c)} \quad (8)$$

We applied this equation to both the XAD-7-phenol and XAD-4-*p*-chlorophenol systems at 303 K. The relative deviations between experimental and calculated data were 11.6% for the former system and 14.3% for the latter. The deviations are much larger than those in the case of the equation of Jossens *et al.* As shown in Fig. 5, for example, this poor fitting accuracy is due to a systematic deviation. That is, the calculated values are lower than the experimental ones in both the regions of lower and of higher concentration, while in the region of medium con-

centration the calculated values are higher than the experimental ones. Thus, it is evident that Eq. (8) does not give a good fit to the equilibrium data of MR resins in a concentration range from 10 to 10⁻² mol/m³. The reason seems to be that the energy distribution function of adsorption sites assumed in derivation of Eq. (8) is different from that for MR resins.

2.3 Equation based on a vacancy solution theory

A following equation based on a vacancy solution theory, proposed by Suwanayuen and Danner,¹¹⁾ has four adjustable parameters: q^∞ , H , and Wilson's parameters, Λ_{31} and Λ_{13} .

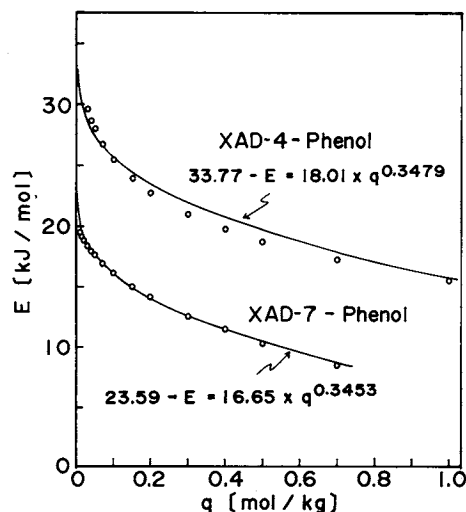


Fig. 4. Dependence of isosteric heat of adsorption on amount adsorbed. Solid lines were calculated from Eq. (2) with the values of P , C , and E_0 in Table 2.

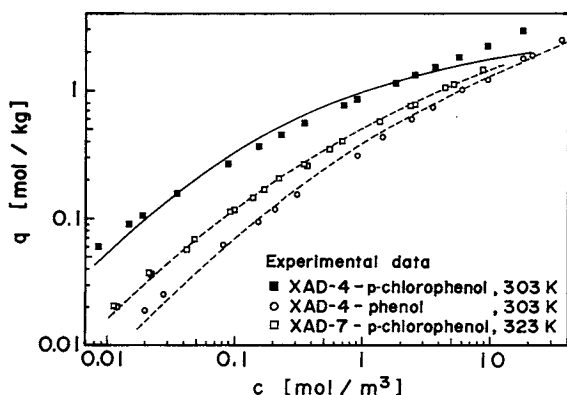


Fig. 5. Comparison between experimental data and results obtained by parameter-fitting. Solid and broken lines represent the equation of Okazaki *et al.* and the equation based on the vacancy solution theory, respectively.

$$c = \left[\frac{q^\infty}{H} \cdot \frac{\theta}{1-\theta} \right] \left[A_{13} \frac{1-(1-A_{31})\theta}{A_{13}+(1-A_{13})\theta} \right] \times \exp \left[-\frac{A_{31}(1-A_{31})\theta}{1-(1-A_{31})\theta} - \frac{(1-A_{13})\theta}{A_{13}+(1-A_{13})\theta} \right] \quad (9)$$

where θ is the fraction coverage of solute (q/q^∞). It has been reported that this equation developed for gas adsorption is applicable to adsorption from dilute solutions on activated carbons.³⁾ As shown in Fig. 5, for example, adsorption isotherms calculated from parameters determined by a least-squares fitting procedure are in fairly good agreement with the experimental data, although the deviation is to some extent similar to that observed for the equation of Okazaki *et al.* Table 3 shows values of the four parameters and the relative deviations. The relative deviations are less than 5% except for the phenol system (8–9%).

Furthermore, the values of q^∞ are comparable to those determined by the equation of Jossens *et al.*, for which the values are about 6 and 3 mol/kg for XAD-4 and XAD-7, respectively. Therefore, this equation gives a fairly good representation for the equilibrium data of MR resins in a concentration range from 10 to 10^{-2} mol/m³. This equation, however, is inferior to that of Jossens *et al.* because there exists a definite systematic deviation as shown in Fig. 5.

More detailed investigation will be necessary because this equation is of advantage in extending application to multi-solute systems.³⁾

2.4 Toth's equation

The following semi-empirical equation, proposed by Toth,¹²⁾ has three parameters: q^∞ , b and M , in which the value of M is a semi-empirical parameter characteristic of the adsorbent only, irrespective of the temperature and the nature of the adsorbate.

$$q = q^\infty c(b + c^M)^{-1/M} \quad (10)$$

By the same method used to obtain the value of P in the equation of Jossens *et al.*, the values of M were determined to be 0.1993 ± 0.0532 and 0.2167 ± 0.0554 for XAD-4 and XAD-7, respectively. Using the value of M , the remaining two parameters were determined by a least-squares fitting procedure. Then, the maximum average relative deviation was 5.59% for XAD-4-phenol system at 323 K, which is slightly larger than that in the case of the equation of Jossens *et al.* However, the values of q^∞ determined increased with an increase in temperature for all systems. Judging from the temperature dependence of the adsorption isotherms, this is unreasonable. Therefore, Toth's equation is not suitable for correlating adsorption from aqueous solutions on MR resins.

2.5 Redlich-Peterson's equation

As a typical example of an empirical isotherm equation, Redlich-Peterson's equation¹⁰⁾ containing three parameters, H , a , and β , has been often used.^{2,5,8,9)}

$$q = Hc/(1 + ac^\beta) \quad (11)$$

This equation gave a good representation for adsorption of phenol from aqueous solutions on Amberlite XAD-8.¹⁾

Applying this equation to the present data, average relative deviations of 0.93–3.36% and 1.71–3.45% for XAD-4 and XAD-7, respectively, were obtained. These relative deviations are almost the same as those in the case of the equation of Jossens *et al.* Therefore, this equation is good for fitting the equilibrium data. However, it has no theoretical basis and, in addition, does not satisfy the thermodynamic boundary condition at highest coverage, because it tends to a Freundlich's equation at higher concentration. Therefore, the equation of Jossens *et al.* seems to be

Table 3. Parameters and relative deviations in the equation based on the vacancy solution theory

Adsorbent	Adsorbate	Temp. [K]	H [m ³ /kg]	q^∞ [mol/kg]	A_{13} [—]	A_{31} [—]	Δq [%]*
XAD-4	Phenol	303	0.8185	6.475	0.2125	4.698	9.00
	<i>p</i> -Chlorophenol	303	8.354	6.239	0.1699	5.892	2.53
	<i>p</i> -Cresol	303	4.295	6.048	0.1892	5.276	4.05
XAD-7	Phenol	303	0.3825	3.548	0.2473	4.037	8.58
	<i>p</i> -Chlorophenol	303	3.626	4.098	0.1962	5.035	4.86
		323	1.751	4.126	0.2160	4.618	4.13
	<i>p</i> -Cresol	303	1.067	5.575	0.2096	4.833	8.67

* See Table 1.

more advantageous than the empirical Redlich-Peterson's equation.

2.6 Adsorption potential theory

Hasanain and Hines⁴⁾ have applied the Polanyi adsorption potential theory to correlate the equilibrium data for adsorption of carboxylic acids from aqueous solutions on Amberlite XAD-2 and have reported that the data for the partially soluble carboxylic acids do not give a single characteristic curve independent of temperature.

In liquid-phase adsorption, the volume adsorbed is plotted against the following adsorption potential per unit volume.^{4,7)}

$$\varepsilon/\bar{V} = \{RT \ln(c_s/c)\}/\bar{V} \quad (12)$$

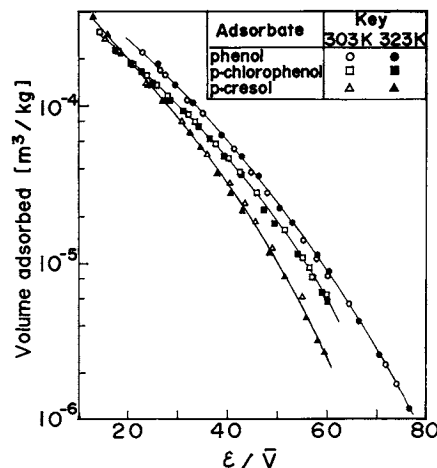
where c_s is the saturated concentration and \bar{V} is the molar volume of the adsorbate. As shown in **Fig. 6**, a single-characteristic curve independent of temperature was obtained for each adsorbate. The same result was also obtained for XAD-7. Therefore, it is suggested that once an adsorption isotherm is measured at a temperature, one can estimate adsorption equilibrium at any different temperature by using both the density and the saturated concentration of the adsorbate.

Conclusion

The equation of Jossens *et al.* gave a satisfactory representation for adsorption equilibrium from aqueous solution of phenol and its derivatives on MR resins in a concentration range from 10 to 10⁻² mol/m³ at 273–323 K. The thermodynamical soundness of the equation was verified experimentally for the first time. An equation based on the vacancy solution theory also gave a fairly good representation, though showing a systematic deviation.

Nomenclature

A	= coefficient of Eq. (1)	[(kJ/mol) ^{-1/P}]
a	= parameter in Eq. (11)	[(m ³ /mol) ^{β}]
b	= parameter in Eq. (10)	[(mol/m ³) ^{M}]
C	= coefficient related to the distribution of energy sites on the surface in Eq. (2)	[kJ·kg ^{P} /mol ^{$P+1$}]
c	= bulk concentration	[mol/m ³]

**Fig. 6.** Volume adsorbed as a function of adsorption potential for phenol, *p*-chlorophenol and *p*-cresol on XAD-4.

c_s	= saturated concentration	[mol/m ³]
E	= isosteric heat of adsorption	[kJ/mol]
E_0	= isosteric heat of adsorption at infinite dilution	[kJ/mol]
H	= Henry's law constant	[m ³ /kg]
K	= parameter in Eq. (3)	[(kg/mol) ^{P}]
k_{\max}	= maximum adsorption energy level in Eq. (8)	[m ³ /mol]
k_{\min}	= minimum adsorption energy level in Eq. (8)	[m ³ /mol]
M	= parameter related to inhomogeneity characterizing the adsorbent in Eq. (10)	[—]
P	= parameter related to the distribution of energy sites on the surface in Eq. (2)	[—]
q	= amount adsorbed	[mol/kg]
q^∞	= ultimate amount adsorbed	[mol/kg]
R	= gas constant	[kJ/mol·K]
T	= absolute temperature	[K]
\bar{V}	= molar volume of solute	[m ³ /mol]
α	= $(1-P)/P$	[—]
β	= parameter in Eq. (11)	[—]
A_{13}, A_{31}	= Wilson's parameters for interaction between water and solute in adsorbed phase	[—]
θ	= fraction coverage of solute (= q/q^∞)	[—]
ε	= adsorption potential	[kJ/mol]

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A RATE ANALYSIS FOR OXIDATION OF POROUS REDUCED IRON WITH WATER VAPOR

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Steam oxidation of porous reduced iron, prepared by hydrogen reduction of iron oxide sintered with inert silica, was carried out under conditions of temperature 460–700°C and steam partial pressure 0.002–0.02 MPa. The oxidation reaction could be represented by a two-stage reaction. In the first stage, iron is oxidized to magnetite. After the completion of the first-stage reaction, magnetite is slowly oxidized to hematite. In the first-stage oxidation reaction, which is the main reaction to produce hydrogen, the initial activity of solid material did not change in the reduction-oxidation cyclic operation. The initial conversion rate could be represented by a Langmuir-Hinshelwood type equation containing the adsorption term of water vapor.

Introduction

It has been known that hydrogen gas can be obtained from the reducing lean gas in the effluent from industrial facilities such as reduction furnaces by the principle of the Steam Oxide Process^{1,6,10,11,14–16} which uses the redox cycles of metal oxide and water vapor.

The reduction kinetics of iron oxide has been investigated by many workers.^{3,7–9,12} However, the complete oxidation kinetics of reduced iron to hematite as a reverse reaction has not yet been reported. Though Turkdogan *et al.*^{17,18} have investigated the oxidation of reduced iron to wustite in water vapor, the detailed kinetics involved in this redox process has not been discussed.

In this work, the oxidation of reduced iron with water vapor was carried out until the iron is oxidized to hematite, and the progress of reaction in this system was examined. Also, the effect of cyclic operation on the reactivity of solid material was investigated.

1. Experimentals

1.1 Materials

The reactant solid is a calcined mixture of reduced iron and inert silica prepared by the procedures described in the previous paper.¹³

The pore volume and pore surface area of the sample particles were measured by a mercury porosimeter (Porosimetro series 1500, Carlo Erba) and a BET apparatus with nitrogen as adsorption gas, respectively. Physical properties of the original sample solid are listed in Table 1.

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