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Adsorption Equilibrium Data for Substituted Phenols on Activated Carbon

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Adsorption equilibria for 24 phenols were studied on Filtrasorb-400 activated carbon at 30 ± 2 °C. The Freundlich constants *k* and *n* were determined. A new model was developed using a thermodynamic approach, and an equation was obtained which is similar to the Freundlich model with constants *J* and *m*. The constant *J* was correlated against the number of carbon atoms in the adsorbate and its measured solubility in water. The correlation resulted in a division of the phenols into two groups: polar molecules and nonpolar molecules, which showed opposite behavior with respect to the activity coefficient of the adsorbed molecule as interpreted from their Freundlich isotherms.

Introduction

The adsorption of organic matter onto activated carbon has emerged as the most economical and efficient method for the treatment of hazardous industrial waste. Phenolic compounds are classified by the Environmental Protection Agency (EPA) as priority pollutants. These compounds impart objectionable taste and odor to drinking water at concentrations as low as 0.005 mg/L. Adsorption of phenols on activated carbon has, therefore, emerged as a promising process. Determination of the adsorption equilibrium isotherm is a primary activity in developing an adsorption-based process. Generally few data are available which give complete isotherms for a class of compounds on the same carbon.

In this paper, adsorption equilibria of 24 phenols have been studied on one carbon. An attempt has been made to correlate the experimental data with molecular parameters, with a view to understanding the process of adsorption of phenols on activated carbon.

Literature Survey

Mattson et al. (*1*) observed a hysteresis during the adsorption of phenol which they attributed to irreversible adsorption of phenol on carbon. They also suggested that the adsorption may follow a donor-acceptor mechanism involving carbonyl oxygens of the carbon surface acting as electron donor and the aromatic ring of the solute as an acceptor.

Zogorski et al. (*2*) observed that the kinetics of phenol adsorption depends on the adsorbent particle size, hydronium ion concentration, and adsorbate concentrations. They showed that the adsorption of phenols was extremely rapid. Approximately 60-80% of the adsorption occurred within the first hour of contact.

Peel and Benedek (*3*) reported that, for granular activated carbon, the equilibrium time was up to 3 weeks with phenol and up to 5 weeks with *o*-chlorophenol, but for powdered carbon only 3-5 days of equilibrium time was required. Up to 80% of the adsorption equilibrium was reached in the first few hours while the remaining capacity was utilized very slowly.

In the published literature some attempts have been to interpret the adsorption data. Many of these attempts have been directed at predicting multisolute adsorption from single solute data. Abe et al. (*4*) have correlated the adsorbability of 93 organic compounds at a single liquid-phase concentration against various physical parameters like molecular weight, molar attraction constant, modified organicity/inorganicity, molar refraction, and polarity. They have suggested that the adsorption of the solute in the aqueous phase involves precipitation of the hydrocarbon portion of the molecule and that it depends on the volume of the hydrocarbon. However, they have studied very few phenols, and most of the molecules are aliphatic.

Table I. Characteristics of Filtrasorb-400 Grade Carbon Used

total surface area (N_2, BET[a] method)	1000-1200 m^2/g
bulk density	432 kg/m^3
particle density wetted in water	1300-1400 kg/m^3
pore volume	95×10^{-5} m^3/kg
iodine number	1050 min
abrasion number	78 min
moisture content	0.9%
water-soluble ash (max)	0.5%

[a] Brunauer-Emmett-Teller.

Chitra and Govind (*5*) developed a group contribution method for estimating the Freundlich constants *k* and *n* for a variety of adsorbates. A thermodynamic model based on the ideal liquid phase was used to obtain group contribution parameters. These group contributions represented solute-solvent and solute-adsorbent interactions jointly. No aromatic molecules or phenols appear to be included in their study.

Belfort (*6*) used solvophobic interaction theory with simplifying assumptions for correlating the molar adsorption capacity of different single organic solutes on activated carbon from dilute aqueous solutions.

Nirmalakhandan and Speece (*7*) have used molecular descriptors such as molecular connectivity indices and modified polarizability factors, which can be calculated from the molecular structure of the adsorbate, to predict the adsorbability defined as ln ($Q°b$) in accordance with Belfort (*6*). However, it must be noted that their data were obtained at a controlled pH using a phosphate buffer. Applicability of these data in industrial systems would, therefore, be restricted.

Dobbs et al. (*8*) have used octanol/water partition coefficients and modified Randic indices to correlate the adsorption data in terms of partition coefficients which were defined as the ratio of the concentration of the effluent in the solid phase and the concentration in the liquid phase. However, their correlation was established for wastewater solids collected from municipal wastewater effluent plants and not on activated carbon, and none of the compounds studied were aromatic.

Experimental Section

Materials. Filtrasorb-400 activated carbon (Calgon Corp.) ground to 95-μm size was used as adsorbent. The powdered carbon was washed with boiling distilled water 6-7 times, dried at 120 °C for 3 h, and stored in a desiccator. The specifications of the activated carbon are given in Table I. The phenols used in the study were of analytical reagent grade supplied by Loba Chemie.

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Table II. Values of ln J, m, and ln X_{am} and Solubilities

compd	ln J	m	ln (X_{am}/(mol/g of carbon))	solubility (mole fraction)
Group A				
phenol	−3.161	4.002	−4.548	1.561×10^{-2}
o-chlorophenol	−3.910	5.356	−4.705	3.105×10^{-3}
m-chlorophenol	−3.552	5.227	−4.685	3.475×10^{-3}
p-chlorophenol	−3.955	4.790	−4.682	3.565×10^{-3}
2,3-dichlorophenol	−6.071	5.165	−4.820	5.180×10^{-4}
2,4-dichlorophenol	−5.824	6.869	−4.820	6.940×10^{-4}
2,5-dichlorophenol	−4.358	5.390	−4.820	3.940×10^{-4}
2,4,6-trichlorophenol	−10.416	5.292	−4.923	6.200×10^{-5}
o-cresol	−4.199	7.417	−4.725	4.552×10^{-3}
m-cresol	−3.871	5.628	−4.718	3.877×10^{-3}
p-cresol	−3.958	5.897	−4.718	3.616×10^{-3}
2,3-dimethylphenol	−4.706	7.396	−4.866	6.180×10^{-4}
2,4-dimethylphenol	−5.958	6.384	−4.868	1.135×10^{-3}
2,6-dimethylphenol	−5.471	8.742	−4.868	1.005×10^{-3}
3,4-dimethylphenol	−4.001	8.620	−4.862	8.930×10^{-4}
3,5-dimethylphenol	−4.327	6.737	−4.865	7.630×10^{-4}
p-isopropylphenol	−7.597	3.908	−5.035	5.070×10^{-4}
Group B				
o-nitrophenol	−8.898	2.205	−4.713	2.570×10^{-4}
p-nitrophenol	−2.453	5.630	−4.713	2.331×10^{-3}
o-methoxyphenol	−1.975	7.593	−4.772	3.589×10^{-3}
p-methoxyphenol	−1.434	12.291	−4.764	6.932×10^{-3}
o-isopropylphenol	−4.934	9.390	−5.041	5.420×10^{-4}
2,6-dichlorphenol	−3.597	7.638	−4.815	2.350×10^{-4}
o-hydroxybenzoic acid	−5.185	2.846	−4.750	9.130×10^{-4}

Procedure. Adsorption Isotherm. Adsorption isotherm experiments were carried out with a known amount (100 mL) of specific initial concentration of phenol solution in 10–12 Erlenmeyer flasks to which different weighed carbon quantities were added. The flasks were kept on a rotary shaker (300 rpm) at room temperature (30 ± 2 °C). After the equilibrium was reached (8 days), the samples were filtered through Whatman filter paper no. 5, and the filtrate was analyzed for the residual phenol content using 10-mm silica cells in a Perkin-Elmer 3B UV-visible spectrophotometer at the corresponding maximum absorption wavelengths. The accuracy was 0.5 mg/L, and the detectability was down to 10 mg/L.

Solubility. Experiments were carried out with sparingly soluble phenols (2,4-dichlorophenol and 3,4-dimethylphenol) to check whether 2 h was sufficient for determining the solubility. To five 250-mL beakers containing 100 mL of distilled water each was added an excess of phenol, and the liquid was agitated with a magnetic stirrer. The contents of the beakers were sampled at intervals of 15, 30, 60, 90, and 120 min. The concentration of the phenols in water remained constant after 60 min of agitation. To ensure saturation, the agitation time was fixed at 2 h. In the case of solids, excess phenol was added to 100 mL of distilled water in a 250-mL beaker and stirred with a magnetic stirrer for 2 h. After the saturation, a sample of decanted water was filtered through Whatman filter paper no. 5 and the concentration of the filtrate was measured with a UV–visible spectrophotometer. In the case of a liquid, excess phenol was stirred in a separating funnel, allowed to settle for a long time, and further filtered to remove any organic droplets. The concentration of the phenol was determined by the UV–visible spectrophotometer described earlier. All the solubility measurements were carried out at a temperature of 30 ± 2 °C. The solubilities are given in Table II.

Results

The Freundlich isotherm equation, $x/m = kc^{1/n}$, was fitted to the equilibrium data. The values of k and n for the 24 phenols are listed in Table III.

In alkylphenols and chlorophenols it is observed that the adsorption increases with increasing number of substituents. Thus, dimethylphenols (xylenols) show higher adsorption than methylphenols (cresols). For chlorophenols the adsorption is in the order 2,4,6-trichlorophenol > dichlorophenols > chlorophenols. This can be attributed to the decrease in solubility in water as the number of substituents increases. Also note that with an increase in side chain length the adsorption increases. Thus, isopropylphenol shows a higher adsorption than cresols.

Table III. Freundlich Constants k and n

compd	Freundlich parameters	
	k	n
phenol	89.43	0.1912
o-chlorophenol	182.1	0.1547
m-chlorophenol	169.1	0.1579
p-chlorophenol	159.1	0.1668
2,3-dichlorophenol	265.2	0.1590
2,4-dichlorophenol	360.2	0.1267
2,5-dichlorophenol	236.16	0.1416
2,6-dichlorophenol	318.02	0.1122
2,4,6-trichlorophenol	588.7	0.1512
o-cresol	255.9	0.1121
m-cresol	167.7	0.1476
p-cresol	181.4	0.1476
2,3-dimethylphenol	217.64	0.1287
2,4-dimethylphenol	253.3	0.1329
2,6-dimethylphenol	326.3	0.1068
3,4-dimethylphenol	283.6	0.1010
3,5-dimethylphenol	218.1	0.1272
o-nitrophenol	147.8	0.3020
p-nitrophenol	166.5	0.1494
o-methoxyphenol	233.14	0.1029
p-methoxyphenol	337.0	0.0777
o-isopropylphenol	320.0	0.0880
p-isopropylphenol	175.8	0.1905
o-hydroxybenzoic acid	86.36	0.2468

Table III indicates that the nature of the substituents also affects the adsorption. Hence, *o*-isopropylphenol shows a higher adsorption than *o*-hydroxybenzoic acid. The order of adsorption can be given as follows: isopropyl > methoxy > methyl > chloro > nitro. Isomers showed a significant dissimilarity in adsorption isotherms.

Interpretation of Results by an Adsorption Model

The above observations suggest the existence of a relation between adsorption isotherms of different phenols, particularly those belonging to a homologous series. These interrelationships between the Freundlich isotherms for different phenols on the same active carbon were studied, and a simplified thermodynamic equilibrium model was developed with the following assumptions.

(i) Water is assumed to be a nonadsorbable species for the activated carbon.

(ii) Every carbon atom on the surface of the activated carbon has been assumed to be a potential site for adsorption. The concentration of the active sites on the surface can be expressed as a number per gram of carbon. For a carbon of 1000 m^2/g surface area, and assuming a C–C distance of 1.42 Å in a hexagonal lattice, this concentration is 3.8×10^{22} sites/g of carbon.

(iii) The liquid phase was assumed to be a dilute binary solution of adsorbate in water. Activity coefficients of the adsorbate in aqueous solution have been equated to the infinite dilution activity coefficient of the adsorbate.

(iv) For simplicity, the adsorbed phase has been treated as a dilute homogeneous solution of sorbate with active sites. Typically, for phenol, the maximum loading is 6.7 mmol/g of carbon. This corresponds to about nine sites per molecule of phenol. Thus, the maximum value of the concentration of the sorbate in solution with active sites is 10%. For all other loadings this concentration is less than 10%. Lacking an adequate description of the adsorbed phase, this assumption could be accepted as a starting point.

(v) The activity coefficient of the adsorbate in solution with active sites has been taken to be a constant corresponding to an infinite dilution activity coefficient. The standard-state free energy of the sorbate in solution phase and sorbed phase is considered to be the same for simplicity.

(vi) The infinite dilution activity coefficient of phenol in solution is assumed to be proportional to the solubility as $\gamma_{al}^{\infty} = \beta S_a^{\,r}$.

(vii) The interactions of the adsorbate with the active sites cannot be easily described. It has been assumed that the active sites (which are responsible for adsorption) are reduced in their effectiveness as the adsorption proceeds. Physically this could be interpreted as an increase in the mean distance between any molecule selected at random and the adsorbing surface. Mathematically this is assumed to be expressed as a reduction in the number of active sites for adsorption as per the following expression:

$$(\alpha/\alpha_0) = (X_a/X_{am})^{-m}$$

where α is the number of active sites at a loading of X (mol/g of carbon), X_{am} is the maximum possible loading of the adsorbate on carbon, and α_0 and m are arbitrary constants. X_{am} is assumed to correspond to a situation where the entire pore volume is assumed to be filled with the adsorbate.

Since the purpose of the analysis is to develop an insight into the Freundlich k and n constants, the following model resulting from the above assumptions can be considered as a starting point. As more and more adsorption data are collected and interpreted through various approaches, further refinements should be possible.

With these assumptions and equating partial molar free energies of the adsorbate in the solution phase and the adsorbed phase, it can be shown that the isotherm can be represented as

$$y_a = J[X_a/X_{am}]^{1+m} \qquad (1)$$

$$J = \frac{\gamma_{as}^{\infty}}{\gamma_{al}^{\infty}} \frac{X_{am}}{\alpha_0}$$

or

$$\ln (J/X_{am}) = \ln \gamma_{as}^{\infty} - \ln \gamma_{al}^{\infty} - \ln \alpha_0 \qquad (2)$$

The infinite dilution activity coefficient for the solute in solution γ_{al}^{∞} is represented in a simplified way as $\gamma_{al}^{\infty} = \beta S_a^{\,r}$.

The infinite dilution activity coefficient for the adsorbate cannot be conveniently represented due to lack of a model. Therefore, the model of Pierotti et al. (*9*) for dilute solutions was extended to solids as follows. From ref 9

$$\log \gamma_1^{\infty} = A_{12} + B_2(N_1/N_2) + C_1/N_1 + D_0(N_1 - N_2)^2 + F_2/N_2 \qquad (3)$$

where subscripts 1 and 2 refer to solute and solvent, respectively. A–F are constants dependent on the nature of the functional groups of the solute, solvent, both, or neither, as indicated by the subscripts 1, 2, 12, and 0.

The number of carbon atoms of the solvent molecule cannot be defined for an activated carbon surface. However, assuming that the number of carbon atoms that come into play is proportional to the number of carbon atoms on the solute molecule, we get

$$N_2 = k_1 N_1 \qquad (4)$$

Substituting eq 4 in eq 3 and rearrangement gives

$$\log \gamma_{as}^{\infty} = [A_{12} + B_2/k_1] + [C_1 + F_2/k_1](1/N_1) + [D_0(1 - k_1)^2]N_1^2$$
$$= P + Q/N_1 + RN_1^2 \qquad (5)$$

In the above formulation constants P, Q, and R would depend on both adsorbate and adsorbent.

In eq 2 further substituting for $\gamma_{al}^{\infty} = \beta/S_a^{\,r}$ and substituting eq 5 in eq 2 yield

$$\ln (J/X_{am}) = (P - \ln \alpha_0 - \ln \beta) + Q/N_1 + RN_1^2 - \ln S_a \qquad (6)$$

The data available were used to verify this kind of dependence.

Correlation for ln J. Using eq 1, ln J values were calculated from the adsorption equilibrium data. The values of ln J are shown in Table II. The values of ln J and X_{am} were used to obtain a correlation between the number of carbon atoms (N) and the solubility of the adsorbate in water using eq 6. While considering the number of carbon atoms, the carbon atoms attached to chlorine were not taken into account, since the chlorine atom is much bigger than the carbon atom and, therefore, the carbon atom is considered to be ineffective for the adsorption process. When all the phenols were correlated together, the correlation coefficient was poor (0.529), though statistically significant. However, grouping these phenols in two groups as shown in Table II and correlating separately improved the correlation coefficient. Group A contains phenol, cresols, xylenols, di- and trichlorophenols, and *p*-isopropylphenol, whereas group B contains phenols which are strongly polar with intra- or intermolecular hydrogen bonding. In group A, an interaction parameter I was included for the distinguishing behavior of the $-CH_3$ group in their contribution to the differences in the adsorption behavior of different xylenols. Therefore, when ln J was correlated against the number of carbon atoms and the solubility, the following equation was obtained for group A:

$$\ln (J/X_{am}) = 22.56 - 96.83/N - 0.23N^2 - 0.63 \ln S_a - 0.85I$$

I is the interaction parameter which is zero for cresols and chlorophenols, and is equal to the number of methyl groups ortho or para to the hydroxyl minus one for xylenols. For the above correlation, the correlation coefficient was 0.936. All coefficients were also significant at 90% confidence level.

For group B the following equation was found to hold:

$$\ln (J/X_{am}) = -7.29 + 105.6/N + 0.17N^2 + 2.46 \ln S_a$$

The correlation coefficient was 0.969. Graphs comparing the observed and the predicted values of ln (J/X_{am}) for groups A and B are shown in Figures 1 and 2, respectively.

Attempts were made to correlate ln (J/X_{am}) against the molecular connectivity indexes and polarizability as used by Nirmalakhandan and Speece (*6*). However, the correlation was not successful. The above researchers have used a Langmuir model for correlation, whereas in this paper an empirical exponential model similar to the Freundlich equation was used.

From the correlation it is observed that the sign of the constants P, Q, and R are opposite which suggests that these two classes of adsorbates behave quite differently. The interaction of the adsorbate with the solvent and the adsorbent is very important in order to understand the phenomenon of adsorption. It is necessary to develop further an explanation for the magnitude of the terms γ_{as}^{∞} and m.

Conclusions

(1) Adsorption of phenols on activated carbon depends on the number and type of substituents.

(2) Carbon atoms attached to chlorine atoms in chlorophenols do not seem to interact with the active sites.

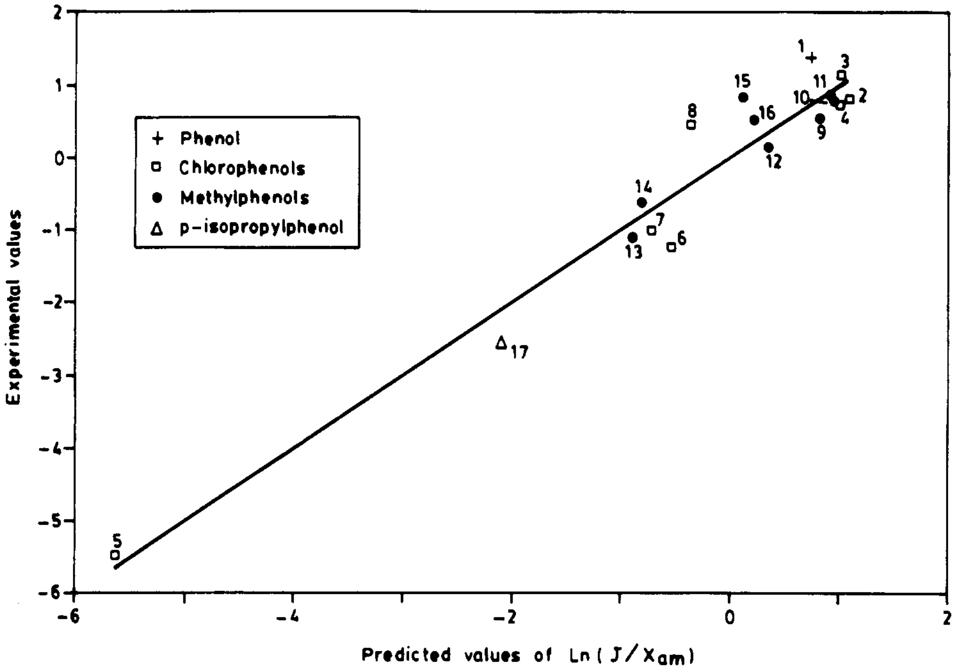

Figure 1. Correlation of ln (J/X_{am}) for group A phenols: (1) phenol, (2) *o*-chlorophenol, (3) *m*-chlorophenol, (4) *p*-chlorophenol, (5) 2,4,6-trichlorophenol, (6) 2,3-dichlorophenol, (7) 2,4-dichlorophenol, (8) 2,5-dichlorophenol, (9) *o*-cresol, (10) *m*-cresol, (11) *p*-cresol, (12) 2,3-dimethylphenol, (13) 2,4-dimethylphenol, (14) 2,6-dimethylphenol, (15) 3,4-dimethylphenol, (16) 3,5-dimethylphenol, (17) *p*-isopropylphenol.

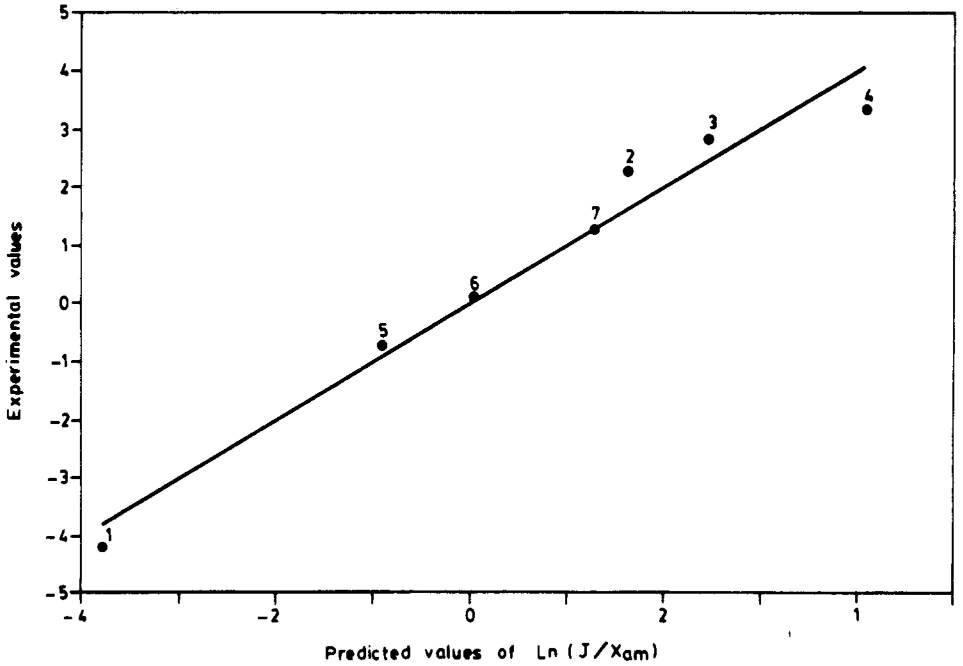

Figure 2. Correlation of ln (J/X_{am}) for group B phenols: (1) *o*-nitrophenol, (2) *p*-nitrophenol, (3) *o*-methoxyphenol, (4) *p*-methoxyphenol, (5) *o*-hydroxybenzoic acid, (6) *o*-isopropylphenol, (7) 2,6-dichlorophenol.

(3) In xylenols with more than one methyl group at the ortho or para position with respect to the hydroxyl group, an interaction parameter is necessary to distinguish the behavior of the methyl group toward adsorption.

(4) To understand the phenomena of adsorption, an insight into the interactions of adsorbate with adsorbent and adsorbate with solvent are necessary.

Glossary

$A,B,C,$ D,F	constants defined as in eq 3
c	concentration of solute in liquid phase at equilibrium
J	constant as defined in eq 1, dimensionless
K	constant from Freundlich equation
k	constant as defined in eq 4
m	constant as defined in eq 1, dimensionless
N	number of carbon atoms
n	constant from Freundlich equation
P,Q,R	constants as defined in eq 5
r	solubility coefficient
S	solubility of the adsorbate
X	concentration of adsorbates in carbon
x/m	amount of adsorbate adsorbed per unit weight of adsorbent
y	composition of liquid phase in mole fraction

Greek Letters

α	concentration of active sites per gram of carbon
β	constant as defined in eq 6
γ	activity coefficient

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Subscripts

a	adsorbate
l	liquid phase
m	maximum concentration
s	solid phase
1	solute
2	solvent
12	solute and solvent
0	independent of solute and solvent

Superscripts

°	standard state
∞	infinite dilution

Registry No. Phenol, 108-95-2; *o*-chlorophenol, 95-57-8; *m*-chlorophenol, 108-43-0; *p*-chlorophenol, 106-48-9; 2,4,6-trichlorophenol, 88-06-2; 2,3-dichlorophenol, 576-24-9; 2,4-dichlorophenol, 120-83-2; 2,5-dichlorophenol, 583-78-8; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5; 2,3-dimethylphenol, 526-75-0; 2,4-dimethylphenol, 105-67-9; 2,6-dimethylphenol, 576-26-1; 3,4-dimethylphenol, 95-65-8; 3,5-dimethylphenol, 108-68-9; *p*-isopropylphenol, 99-89-8; *o*-nitrophenol, 88-75-5; *p*-nitrophenol, 100-02-7; *o*-methoxyphenol, 90-05-1; *p*-methoxyphenol, 150-76-5; *o*-hydroxybenzoic acid, 69-72-7; *o*-isopropylphenol, 88-69-7; 2,6-dichlorophenol, 87-65-0; carbon, 7440-44-0.

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Vapor–Liquid Equilibria in the Systems of Toluene/Aniline, Aniline/Naphthalene, and Naphthalene/Quinoline

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Vapor–liquid equilibria for the aniline/naphthalene, toluene/aniline, and naphthalene/quinoline systems have been determined at 0–1500 kPa and 490–623 K by using a static equilibrium cell. The data can be accurately correlated with the modified Peng–Robinson equation of state by using density-dependent mixing rules. The binary interaction parameters and correction factors for the equation of state are reported at each isotherm. The presence of coal-derived solids in these binary systems did not influence any of the binary bubble pressures.

Introduction

Thermodynamic property correlations and equations of state have been developed for the petroleum industry largely on the basis of measurements in highly paraffinic systems. However, the liquids produced in coal liquefaction are highly aromatic and may contain heteroatoms such as sulfur, oxygen, and nitrogen. Since there is a scarcity of vapor–liquid equilibrium data for mixtures containing aromatic or heterocyclic compounds, additional data on such systems are needed.

Our goal of this study is to obtain vapor–liquid equilibria (VLE) data for model mixtures, representative of coal-derived liquids. Such compounds include polycyclic aromatics, cyclic alkanes, and compounds containing heteroatoms. These results contribute to a data base for aromatic compounds which may be present in coal liquefaction processes (*1–13*) so that coal liquids processing equipment can be accurately designed. A second goal of the study is to determine if the separation of coal liquids by distillation might be affected by the differential adsorption of these compounds on the solids (insoluble organic matter and ash) which may be present in coal liquefaction streams (*14*). The effect of the adsorption can be studied through measurement of the properties of heavy liquid model compounds with and without coal solids. Any variation of bubble pressure of a binary liquid mixture upon the addition of solids can reflect the preferential adsorption of one of the components of the liquid.

Experimental Section

The following list of chemicals were available with a purity of 99% or greater. Aldrich supplied toluene (27,037; 99.9+%), naphthalene (18,450; 99+%), aniline (24,228-4; 99.5+%), and quinoline (25,401-0; 99%). The purity of all chemicals, as measured by gas chromatography (Hewlett-Packard 5880A), was greater than 99%. All chemicals were used without further purification.

The coal solids were obtained from Gulf Research and Technology Center (Extracts P-99-65-25 Vacuum Coal Bottoms). The charcoal, a model coal solid, was available from Aldrich (24,227-6; Darco). Coal solids were extracted by a tetrahydrofuran (THF) solvent in a Soxhlet extraction unit to remove all organic compounds which may be adsorbed on the coal solid surface and to leave a solid composed of ash and insoluble organic matter (IOM). This ensures that any vapor pressure deviation which may result is not due to the extraction of organic compounds from the solid.

The experimental apparatus has been described previously (*15*). Prausnitz et al. measured the vapor–liquid equilibrium of a coal-derived mixture by using a recirculating still which can measure vapor and liquid composition without condensation (*16*, *17*). However, in this study a stainless steel static equilibrium cell with a volume of 70 mL was used to determine the vapor–liquid equilibria and the effect of the differential adsorption of coal-derived mixtures on the solids. A sample of pure or binary liquid was gravimatically mixed and analyzed by GC and then charged to the evacuated stainless steel vessel such that the vapor space was quite small (5–20 mL). The vessel was then immersed in a high-temperature sand bath. The

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